COMPETITIVE PHENYLATION
OF POLYFLUOROBENZENES

by

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To My Parents

and

John.

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I would also like to thank Professor Williams and Bedford College for the offer of a Tutorial Research Studentship.

Finally, I wish to thank all the members of the Chemistry Department who have helped me and encouraged me during my stay here.

ABSTRACT

Benzoyl peroxide was allowed to decompose at $80^{o}c$ in a range of polyfluorobenzenes, (i) in the absence of additives, (ii) in the presence of ferric benzoate, and (iii) in the presence of trichloroacetic acid. The yields of polyfluorobiphenyls and polyfluorophenyl benzoates from these reactions have been measured.

Biaryls arising from displacement of fluorine as well as hydrogen were observed, phenyldehydrogenation occuring more readily than phenyldefluorination in all solvents. Ferric benzoate was found to have only a minimal effect on the yields of biaryls and trichloroacetic acid was found to have no effect. The relative rates of displacement, as shown by the isomer distributions, were found to deviate from those predicted from partial rate factors for the phenylation of fluorobenzene. The effect is more pronounced with increase fluorine substitution.

The esters were found to arise from fluorine displacement only. Their yields decreased with added ferric benzoate and increased with added trichloroacetic acid.

The identity of some of the products from the residues arising from the decomposition of benzoyl peroxide in 1,3,5-trifluorobenzene and 1,2,3,4-tetrafluorobenzene was investigated.

Competitive phenylation reactions have been carried out in binary mixtures of polyfluorobenzenes. The relative susceptibilities of each substrate were measured by the relative yields of the appropriate biaryls. The orientation of attack was unaffected by the presence of a second substrate except when hexafluorobenzene was present. Then, the selectivity of phenylation, as judged by the change

of orientation, apparently increased. However, self-consistent substituent rate factors were not obtainable for any set of competition reactions. Explanations have been suggested to account for these observations.

The steam-volatile products form the thermolysis of phenylazotriphenyl methane (PAT) at 80°, in hexafluorobenzene have been investigated. Some products from the decomposition of benzoyl peroxide (80°)in benzene, pentafluorobenzene and hexafluorobenzene in the presence of pentafluoronitrosobenzene have also been studied.

CONTENTS

I. INTRODUCTION

I. 1 Homolytic Aromatic Arylation

Homolytic arylation involves the replacement of an atom (usually hydrogen), situated at an aromatic nucleus, by an aryl radical. These reactions have been of interest because of (a) their potential synthetic usefulness and (b) their contribution to the understanding of the chemistry of free radicals. They have been extensively studied and several reviews have been published.[1-8]

There are a number of reactions whereby homolytic arylation can be effected. These include the decomposition of many types of azo- and diazo-compounds such as aryl iodides. The most widely studied homolytic arylation reaction is, however, the decomposition of benzoyl peroxide. This reaction provides the 'cleanest', most convenient source of phenyl radicals and, under the best conditions, gives higher yields of products than other sources.

I. 2. Homolytic Aromatic Substitution with Benzoyl Peroxide

2.1 Mechanistic Studies

The decomposition of benzoyl peroxide in aromatic solvents results in the formation of biaryls. In 1925 Gelissen and Hermans[9] showed that, as well as biaryls, the products included carbon dioxide and benzoic acid. Considerable amounts of high-boiling resinous material is also formed. The conclusion that, in general, the biaryls formed are those in which one aryl group is derived from the peroxide, and the other from the substrate has been confirmed by subsequent work.[10-13] In 1937 Hey and Waters[1] rationalized this observation in terms of attack of aryl radicals on the substrate.

The presence of small quantities of the aroic esters among the products of these reactions indicates that aroyloxy radicals are intermediates in the formation of phenyl radicals :

$$(\mathrm{ArCO.O})_2 \longrightarrow 2\ \mathrm{ArCO.O}\cdot \qquad (1)$$

$$\mathrm{ArCO.O}\cdot \longrightarrow \mathrm{Ar}\cdot + \mathrm{CO_2} \qquad (2)$$

Studies of the reaction in the presence of inhibitors[14-18] have confirmed this reaction path.

Under most conditions only the unsymmetrical biaryl is formed, so it follows that hydrogen abstraction from the nucleus of the substrate does not occur, and that biaryls are not formed by the sequence of reactions (3) and (4), since, if they were, the symmetrical biaryl ArAr and Ar'Ar' must necessarily also be formed.

$$\mathrm{Ar}\cdot + \mathrm{Ar'H} \longrightarrow \mathrm{ArH} + \mathrm{Ar'}\cdot \qquad (3)$$

$$\mathrm{Ar}\cdot + \mathrm{Ar'}\cdot \longrightarrow \mathrm{ArAr'} \qquad (4)$$

Traces of the symmetrical biaryl ArAr have only been identified when the decomposition has been carried out at high concentrations of peroxide.[12,19,20] Under such conditions these products are formed by dimerization of the aryl radicals when these are present in high concentration. Symmetric biaryls of the type Ar'Ar' have never been isolated.

The lack of a kinetic isotope effect in the arylation of deuteriated or tritiated aromatic compounds[21-23] indicates that the substitution step proceeds by the addition of an aryl radical to the substrate nucleus to give a σ-complex, the arylcyclohexadienyl radical, which is subsequently dehydrogenated.

$$\mathrm{Ph}\cdot + \mathrm{ArH} \longrightarrow [\mathrm{PhArH}]\cdot \quad (\mathrm{I}) \qquad (5)$$

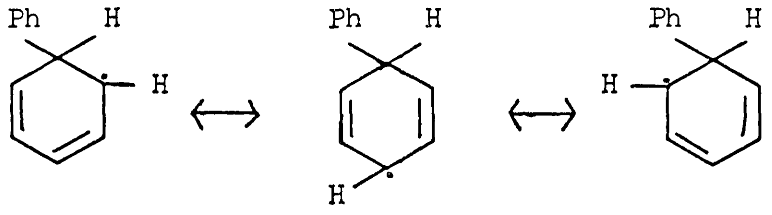
$$[\mathrm{PhArH}]\cdot + \mathrm{R}\cdot \longrightarrow \mathrm{PhAr} + \mathrm{RH} \qquad (6)$$

Hey et al.[23] suggested that the addition step is the rate-determining one with the subsequent loss of hydrogen being the fast stage. Eliel et al.[24] also reported the absence of an isotope effect and suggested that the σ-complex formation is irreversible. This theory has been supported by Jackson,[25] and by Saltiel and Curtis.[26]

Results from recent studies indicate that in some cases the formation of the arylcyclohexadienyl radical could be reversible. Perkins et al.[27] have found evidence for the reversible formation of 2-chlorophenylcyclohexadienyl radical at 210°. Kobayashi et al.[28] reported the observation of an isotope effect in the phenylation of chlorobenzene, nitrobenzene and m-dinitrobenzene in dimethylsulphoxide at 20°. The isotope effect was found to be greatest for the formation of o-substituted biaryls. This observation was explained in terms of reversible addition of phenyl radicals to the substituted benzenes to form arylcyclohexadienyl radicals. However, it has been suggested that the apparent reversibility of phenyl radical addition to aromatic substrates in dimethylsulphoxide arises from the solvent effect of dimethylsulphoxide on free radical behaviour.[27] More recently Nonhebel *et al.*[29,30] claimed to have obtained evidence in favour of the reversible addition of phenyl radicals to di-substituted benzenes, such as xylene and dichlorobenzene, at moderate temperatures (80-120°), particularly when the phenyl radical attacked the substrate at the *o*-position. It has also been reported that in the vapour phase (500°) the addition of phenyl radical to chlorobenzene is reversible.[31]

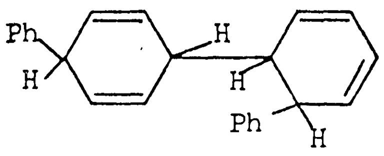
Perkins *et al.*[27], however, had shown that the formation of the 2-chlorophenylcyclohexadienyl radical was not reversible at temperatures below 200° and no unequivocal evidence for the reversibility of phenylation in systems involving aroyl peroxides has been found. Thus, σ-radical formation from the decomposition of benzoyl peroxide at normal temperatures (80-100°) appears to be irreversible.

The decomposition of benzoyl peroxide in aromatic solvents is usually accompanied by the formation of large amounts of high-boiling residue. In 1957, Pausacker and Lynch[32], and Walling[33], independently reported evidence that the σ-radical is a resonance stabilised arylcyclohexadienyl radical (II-IV) which is capable of dimerization and disproportionation.



(II) (III) (IV)

Dimerization of the σ-complex should give, specifically, three isomeric tetrahydroquaterphenyls (V), (VI) and (VII) :



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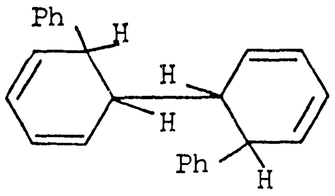

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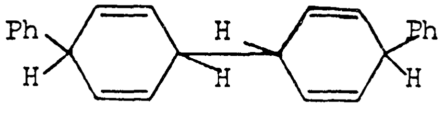
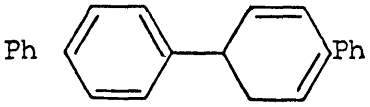


(VIII)

These compounds are the main constituents of the high-boiling residue formed in this reaction.[32]

The complex problem of isolation and identification involved in the investigation of these residues can be simplified by the dehydrogenation of the hydroaromatic compounds to quaterphenyl derivatives. Such dehydrogenation, with o-chloranil, of the involatile products of the reaction of benzoyl peroxide with benzene made possible the identification of the three expected isomers of quaterphenyl.[34]



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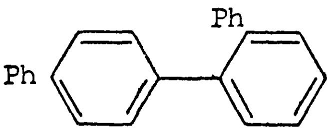

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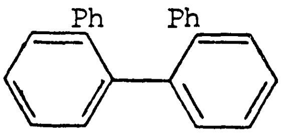

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Evidence for the disproportionation of the σ-complex as in reaction (7) has been presented by De Tar and Long[35], who found 1,4-dihydrobiphenyl to be present as a product from the decomposition of benzoyl peroxide in very dilute solutions in benzene.

$$2[\mathrm{PhArH}]\cdot \longrightarrow \mathrm{PhAr} + \mathrm{PhArH_2} \qquad (7)$$

The involatile residue resulting from the decomposition of benzoyl peroxide in aromatic solvents also contains some terphenyl. That p-terphenyl is formed by the further phenylation of the biphenyl product from the reaction in benzene was established by Razuvaev et al.[36] who found, using $[1\text{-}^{14}C]$benzene, that a small amount of p-terphenyl labelled in one nucleus and a much greater amount of p-quaterphenyl labelled in two benzene rings was obtained.

2.2 Kinetic Studies

It has been firmly established that σ-complexes are intermediates in the arylation process, and kinetic studies have been used to elucidate the mechanisms by which these σ-complexes become dehydrogenated to biaryls. Nozaki and Bartlett[37] established that the decomposition of benzoyl peroxide in a number of solvents, including some aromatic solvents such as benzene, obeys a kinetic law of the form:

$$-d[P]/dt = k_1[P] + k_{1.5}[P]^{1.5} \tag{8}$$

where P represents the peroxide, $k_1[P]$ represents a primary unimolecular mode of decomposition [reactions (1) and (2)], and $k_{1.5}[P]^{1.5}$ represents an induced (chain) decomposition which proceeds concurrently with primary decomposition. This kinetic form is shown by such a system provided the chains are terminated by a dimerization or disproportionation reaction involving like radicals such as eqn. (9) :

$$2\,R\cdot \longrightarrow \text{products} \tag{9}$$

Termination reactions involving unlike radicals [eqn. (10)] necessarily

$$R\cdot + R'\cdot \longrightarrow \text{products} \tag{10}$$

lead to a kinetic law of the form (11), the induced decomposition then being first order with respect to the peroxide $[P]$.

$$-d[P]/dt = k_1[P] + k_1'[P] \qquad (11)$$

The direct oxidation of σ-complexes by benzoyloxy radicals [eqn. (12)] had originally been suggested to explain the formation of biaryl. This reaction is, however, a termination of the form (11)

$$PhArH\cdot + PhCO.O\cdot \longrightarrow PhAr + PhCOOH \qquad (12)$$

and, therefore, cannot occur if the kinetics are of the form represented by eqn. (8). In further investigations[38-42] the value of the rate-constants [eqn. (8)] have been determined by kinetic experiments in the presence and absence of radical scavengers whose purpose is to inhibit the induced decomposition. Correlation of these kinetic results with the variation in the yields of the various products (biaryls, esters, aroic acids, dihydrobiaryls and the residue) with the initial concentration, has allowed the identification of the σ-complex as the most important chain carrier. Reaction (13) is, therefore, the main chain-transfer stage and is one of the reactions in which biaryls and aroic acids are formed.

$$PhArH\cdot + (PhCO.O)_2 \longrightarrow PhAr + PhCOOH + PhCO.O\cdot \qquad (13)$$

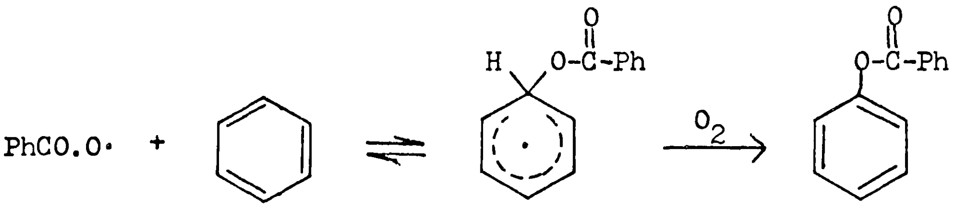
2.3 Benzoyloxylation

A small quantity of ester always accompanies the biaryls in the decomposition of benzoyl peroxide in aromatic substrates. This is thought to be formed by reaction of benzoyloxy radicals with the aromatic substrate to give a σ-complex which is subsequently dehydrogenated [eqn. (14)]; i.e. a reaction analogous to that of phenyl radicals [eqns. (5) and (6)] leading to the formation of biaryls.

$$\mathrm{PhCO.O}\cdot + \mathrm{ArH} \longrightarrow [\mathrm{PhCO.OArH}]\cdot \qquad (14)$$

$$[\mathrm{PhCO.OArH}]\cdot + (\mathrm{PhCO.O})_2 \longrightarrow \mathrm{PhCO.OAr} + \mathrm{PhCOOH} + \mathrm{PhCO.O}\cdot \qquad (15)$$

Nakata, Tokumara and Simamura[43] proposed that the formation of the aroyloxycyclohexadienyl radical in the photolysis of benzoyl peroxide in benzene was reversible since the yield of phenyl benzoate increased with increased concentrations of oxygen.



(16)

The reversible addition theory was substantiated by Saltiel and Curtis[25], although these workers found that the benzoate is formed at the expense of biphenyl in contrast to the report[43] that the benzoate is formed at the expense of benzoic acid. In the thermal decomposition of benzoyl peroxide in aromatic substrates, the ester yield is found to increase on addition of oxidising agents such as oxygen,[24,25,44] copper salts,[45,46] and iodine.[47] Recently physical evidence for the reversibility of aroyloxylation has been obtained from chemically induced dynamic nuclear polarisation (CIDNP) studies, which indicate that the addition of pentafluorobenzoyloxy radicals to chlorobenzene is reversible.[48,49]

Decomposition of benzoyl peroxide in aromatic solvents invariably yields a small amount of phenyl benzoate. Since this is formed even in the presence of iodine, an efficient radical scavanger, Nakata <u>et al</u>.[43] suggested that it is formed within a solvent cage (Scheme 1).

$$(PhCO.O)_2 \longrightarrow (PhCO_2\cdot + PhCO_2\cdot)_{cage} \longrightarrow$$
$$(PhCO_2\cdot + Ph\cdot + CO_2)_{cage} \longrightarrow$$
$$(PhCO_2Ph + CO_2)_{cage} \longrightarrow PhCO_2Ph + CO_2$$

Scheme 1.

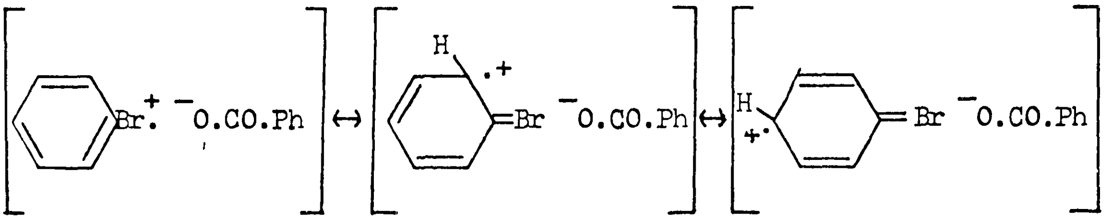
2.4 Deduced Mechanism

Williams et al.[38-42] carried out detailed product and kinetic investigations into the thermal decomposition of benzoyl peroxide in aromatic solvents. From this work they have proposed the following mechanistic scheme to account for their observations, those steps marked with an asterisk being of minor importance.

$$(PhCO.O)_2 \longrightarrow 2\ PhCO.O\cdot \qquad (17)$$
$$PhCO.O\cdot \longrightarrow Ph\cdot + CO_2 \qquad (18)$$
$$Ph\cdot + ArH \longrightarrow [PhArH]\cdot = \sigma\cdot \qquad (19)$$
$$PhCC.O\cdot + ArH \longrightarrow [PhCO.O.ArH]\cdot = \sigma{:} \qquad (20*)$$
$$\sigma\cdot + (PhCO.O)_2 \longrightarrow PhAr + PhCOOH + PhCO.O\cdot \qquad (21)$$
$$\sigma{:} + (PhCO.O)_2 \longrightarrow PhCO.O.Ar + PhCOOH + PhCO.O\cdot \qquad (22*)$$
$$\sigma\cdot + PhCO.O\cdot \longrightarrow PhAr + PhCOOH \qquad (23*)$$
$$\sigma{:} + PhCO.O\cdot \longrightarrow PhCO.O.Ar + PhCOOH \qquad (24*)$$
$$2\ \sigma\cdot \longrightarrow PhAr + PhArH_2 \qquad (25)$$
$$2\ \sigma\cdot \longrightarrow (PhArH)_2 \qquad (26)$$
$$2\ \sigma{:} \longrightarrow \text{oxygen-containing dimerization and disproportionation products} \qquad (27)$$

This work has shown that for the reactions in benzene, alkylbenzenes and fluorobenzene, and in chlorobenzene at low initial peroxide concentrations, the kinetics of the decomposition of benzoyl peroxide obey eqn. (8) (i.e. $-d[P]/dt = k_1[P] + k_{1.5}[P]^{1.5}$).

In these solvents, therefore, reaction (23) is minimal and chains are terminated by dimerization and disproportionation of the σ-complexes. This contention is borne out by an examination of the yields of the various products, since biaryls and dihydrobiaryls are formed by reaction (25), and high yields of the high-boiling residue of such a magnitude as would be predicted from the values of k_1 and $k_{1.5}$, are formed. The reaction in bromobenzene[39], however, has quite different characteristics, since not only do the kinetics obey eqn. (11) (i.e. $-d[P]/dt = k_1[P] + k_1'[P]$) strictly, but the yields of the dihydrobiaryls and of the high-boiling residue are extremely small, while those of the biaryls and of benzoic acid are very high. In this solvent, therefore, the chains are terminated by reaction (23). The reaction in chlorobenzene at high initial peroxide concentrations also conforms to this pattern. The reason for this contrast is thought[39] to be the greater degree of stabilisation of benzoyloxy radicals in bromobenzene by the formation, to a greater extent in this solvent, of charge-transfer conplexes (28), owing to the greater polarisability and electropositivity of the bromine atom.



(28)

The reaction in iodobenzene was studied by Brydon and Cadogan.[50] They found the kinetics to be the same as in bromobenzene; i.e. having a first order induced decomposition.

The reaction in nitrobenzene gives products corresponding to the rate equation (29) at low peroxide concentrations, indicating contributions from both modes of termination, but the kinetics revert to those represented by eqn. (11) at higher concentrations.[41]

$$-d[P]/dt \quad = \quad k_1[P] \quad + \quad k_1'[P] \quad + \quad k_{1.5}[P]^{1.5} \qquad (29)$$

The yields of dihydrobiaryls and of the residue are low. These results indicate the operation of the 'nitro-group effect', discussed later (I. 3.2), which increases the apparent contribution of reaction (21) at the expense of reactions (25) and (26).

I. 3. The Effect of Additives on Phenylation by Benzoyl Peroxide of Aromatic Solvents

3.1 Oxygen

The effect of oxygen in increasing the yield of biaryls at the expense of dihydrobiphenyls and tetrahydroquaterphenyls rather than at the expense of benzoic acid, was first reported by Eberhardt and Eliel.[44] The results were substantiated by subsequent work.[51] It is known that phenyl radicals are not very reactive towards oxygen[52] and, therefore, the oxygen was thought to abstract hydrogen from the σ-intermediate, presumably by the formation of a hydroperoxide radical, which could bring about the oxidation of another σ-radical.

$$[\mathrm{PhArH}]\cdot + O_2 \longrightarrow \mathrm{PhAr} + HO_2\cdot \qquad (30)$$

$$[\mathrm{PhArH}]\cdot + HO_2\cdot \longrightarrow H_2O_2 + \mathrm{PhAr} \qquad (31)$$

Hydrogen peroxide has been detected in these reactions.[53] Some phenol is also formed, and in higher yield at lower temperature.[53] This observation has been attributed to the higher solubility of the gas at lower temperatures and to the more efficient trapping of phenyl radicals by it.

$$\mathrm{Ph}\cdot + O_2 \longrightarrow \mathrm{Ph{-}O{-}O}\cdot \longrightarrow \mathrm{PhOH} \qquad (32)$$

3.2 Nitro-Compounds and other Electron Acceptors

The effect of the presence of nitro-compounds of increasing the yield of biaryls (in phenylation reactions with benzoyl peroxide), was first pointed out by Augood and Williams[3], although the cause of this phenomenon was not clear at the time. It was shown later (a) that only a catalytic amount of a nitro-compound was necessary[54],

(b) that while the yields of biaryls and aroic acid were greatly increased, the formation of residues and of dihydrobiaryls was almost completely suppressed, and (c) that almost all of the nitro-compound could be recovered unchanged at the end of the reaction.[41] The use of this additive in the synthesis of biaryls has been described.[55]

Hall[56] investigated a number of electron-acceptors and showed that all (with the exception of nitromethane) manifest the same 'nitro-group' effect. However, there appears to be no simple relationship between the effectiveness of the additive and its reduction potential.

It is known[57] that the effective catalyst is the corresponding nitoso-compound, which is formed by reduction of the nitro-compound. This conclusion is based on the observations (a) that nitrosobenzene and phenylhydroxylamine (which is converted into nitrosobenzene) are much more effective than nitrobenzene, (b) that the small amount of nitro-compound unrecovered at the end of the reaction would, as nitroso-compound, be sufficient to produce the observed effect, and (c) that e.s.r. spectroscopy reveals the presence of a stable radical, probably a nitroxide, in reactions catalysed by nitro-compounds. The following scheme was proposed to account for the catalytic effect of the nitroso compounds.[57]

$$\mathrm{PhNO_2} \xrightarrow{-[\mathrm{O}]} \mathrm{PhNO} \tag{33}$$

$$\mathrm{Ph}\cdot + \mathrm{PhNO} \longrightarrow \mathrm{Ph_2NO}\cdot \tag{34}$$

$$\mathrm{Ph_2NO}\cdot + [\mathrm{PhArH}]\cdot \longrightarrow \mathrm{PhAr} + \mathrm{Ph_2N.OH} \tag{35}$$

$$\mathrm{Ph_2N.OH} + (\mathrm{PhCO.O})_2 \longrightarrow \mathrm{Ph_2NO}\cdot + \mathrm{PhCOOH} + \mathrm{PhCO.O}\cdot \tag{36}$$

$$\mathrm{Ph_2N.OH} + \mathrm{PhCO.O}\cdot \longrightarrow \mathrm{PhCOOH} + \mathrm{Ph_2NO}\cdot \tag{37}$$

3.3 Metal Salts and Metals

Transition metal compounds, such as copper salts, have also been found to catalyse the oxidation of σ-complexes by benzoyloxy radicals leading to an increase in the yield of biaryl and benzoic acid.[45,46,58] Dailly and Williams[59,60] found that iron(III) benzoate is one of the most efficient metal salts for catalysing the oxidation of the arylcyclohexadienyl radical. They proposed the following scheme to account for their observations.

$$[\mathrm{PhArH}]\cdot + \mathrm{Fe}^{3+} \longrightarrow \mathrm{PhAr} + \mathrm{H}^{+} + \mathrm{Fe}^{2+} \qquad (38)$$

$$\mathrm{PhCO.O}\cdot + \mathrm{Fe}^{2+} \longrightarrow \mathrm{PhCO.O}^{-} + \mathrm{Fe}^{3+} \qquad (39)$$

$$\mathrm{PhCO.O}^{-} + \mathrm{H}^{+} \longrightarrow \mathrm{PhCOOH} \qquad (40)$$

I. 4. Other Sources of Aryl Radicals

4.1 Substances Related to Benzoyl Peroxide

Lead tetrabenzoate has been shown to decompose in aromatic solvents at 125-130° to give biaryls[61], and the sequence of reactions is considered to be :

$$Pb(O.CO.Ph)_4 \longrightarrow Pb(O.CO.Ph)_2 + 2\ PhCO.O\cdot \qquad (41)$$

$$PhCO.O\cdot \longrightarrow Ph\cdot + CO_2 \qquad (42)$$

$$Ph\cdot + ArX \longrightarrow PhArX + [H\cdot] \qquad (43)$$

Phenyl iodobenzoate also gives phenyl radicals on decomposition at similar temperatures[32,62] which may be represented by eqn. (44).

$$PhI(O.CO.Ph)_2 \longrightarrow PhI + 2\ PhCO.O\cdot \qquad (44)$$

The reaction is more complex than this scheme indicates.[63] Although it gives rise to homolytic aromatic substitution, it is by no means a simple replication of the reaction of benzoyl peroxide.

Benzoyloxy, and hence phenyl radicals have also been formed from the thermal decomposition of silver halide dibenzoates.[64]

$$AgX(O.CO.Ph)_2 \longrightarrow 2\ PhCO.O\cdot + AgX \qquad (45)$$

A further source of benzoyloxy radicals is provided by the removal of an electron from the benzoate anion in an electrolytic cell.[65]

$$PhCOO^- \xrightarrow{-e^-} PhCO.O\cdot \longrightarrow Ph\cdot + CO_2 \qquad (46)$$

This method does not lend itself easily to phenylation in non-aqueous media, but the reaction has been successfully used in the phenylation of pyridine.[66]

Aryl radicals have also been formed by the oxidation of aroic acids.[67,68] In all these methods the products are similar to those obtained with benzoyl peroxide.

4.2 Diazo- and Azo- Compounds

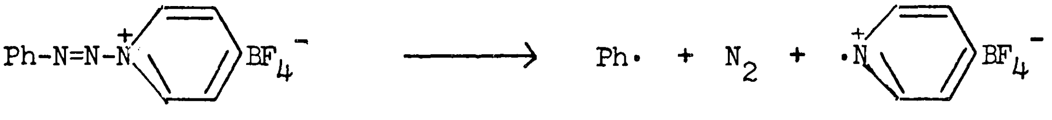
There are many recorded instances of the use of diazo-compounds of various types for the production of aryl radicals for arylation reactions. One of the best known is the Gomberg reaction[69,70] which involves the decomposition of diazoic acids and diazo-esters in heterogenous aqueous aromatic systems.

$$Ar.N_2.OH + Ar' \longrightarrow Ar.Ar'H + N_2 + H_2O \qquad (47)$$

The uses of the Gomberg reaction for preparative purposes have been reviewed.[2,71] Modifications of the original process have been reported.[72-76] The most recent provides a cleaner homogenous system wherein an aromatic amine reacts in situ in an organic solvent with amyl nitrite at 60-80° [77-79]

Another convenient source of aryl radicals is from the diazonium tetrafluoroborates. Abramovitch and Saha[80] found that by the addition of one equivalent of pyridine to the aromatic substrate (in excess) and benzenediazonium tetrafluoroborate, an N-phenylpyridinium tetrafluoroborate is formed (48), which decomposes homolytically to give a phenyl radical (49).

(48)



(49)

Benzenediazonium tetrafluoroborate has also been reduced electrolytically in aprotic solvents to yield the free phenyl radical.[81]

4.3 N-Nitrosoacetanilide

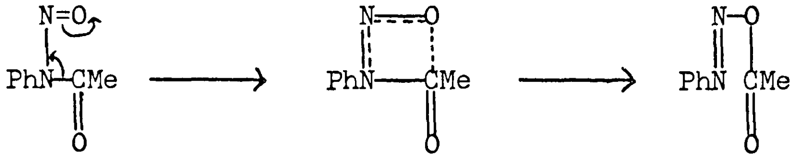
N-Nitrosoacetanilide has been studied extensively as a source of phenyl radicals ever since it was found to decompose easily in benzene at room temperature to give biphenyl and acetic acid (50).[82]

$$C_6H_5N(NO)COCH_3 + C_6H_6 \longrightarrow C_6H_5C_6H_5 + N_2 + CH_3COOH \qquad (50)$$

The subject has been reviewed by Cadogan.[83,84]

The rate of evolution of nitrogen follows a first-order law and is relatively insensitive to the nature of the solvent.[85,86] The rate-determining stage is the rearrangement of the nitroso compound to the diazo-ester (51)[87,88], this rearrangement being effected by nucleophilic attack of the oxygen of the nitroso group on the carbonyl carbon atom (52).[88,89]

$$Ph.N(NO)CO.Me \xrightarrow{slow} Ph.N{=}NO.CO.Me \xrightarrow{PhH/fast} Ph_2 + N_2 + MeCOOH \qquad (51)$$



(52)

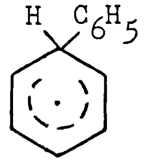
The diazo acetate is apparently in equilibrium with a diazonium acetate ion pair.[90-92]

$$ArN{:}NO{-}COR \rightleftharpoons [ArN_2^{+}\ {}^{-}O.COR] \qquad (53)$$

Simple homolysis of the diazo acetate (54) leading to the oxidation of the intermediate phenylcyclohexadienyl radical by an acetyloxy radical (55), although giving the observed products, has been discounted because the acetyloxy radical is very unstable and fragments to a methyl radical and carbon dioxide very readily[62,93], but the large yields of carbon dioxide are not found in the reaction products.[62,87,94]

$$C_6H_5N{:}NO.CO.CH_3 \longrightarrow C_6H_5\cdot + N_2 + CH_3COO\cdot \qquad (54)$$

$$C_6H_5\cdot + C_6H_6 \longrightarrow$$



$$\xrightarrow{CH_3CO_2\cdot} C_6H_5C_6H_5 + CH_3COOH \qquad (55)$$

Furthermore, in the other reactions of benzene with phenyl radicals products of dimerization and disproportionation of the intermediate phenylcyclohexadienyl radical are formed. In the case of N-nitrosoacetanilide such products are absent, thus suggesting that the required oxidant in this case is very efficient.

Rationalisation of these obstacles in terms of a diffusion-controlled cage mechanism was put forward by Eliel et al.[95], but evidence against this point of view,[96] and for the existence of free phenyl radicals, was later provided.[97]

An apparently complete explanation of the reaction was advanced by Ruchardt and Freudenberg.[98] They proposed a mechanism outlined in Scheme 2, the key step of which involved the stable (π-type) phenyldiazoxyl radical (PhN=NO·), capable of abstracting hydrogen, and thus cleanly oxidising the phenylcyclohexadienyl radical to biphenyl.

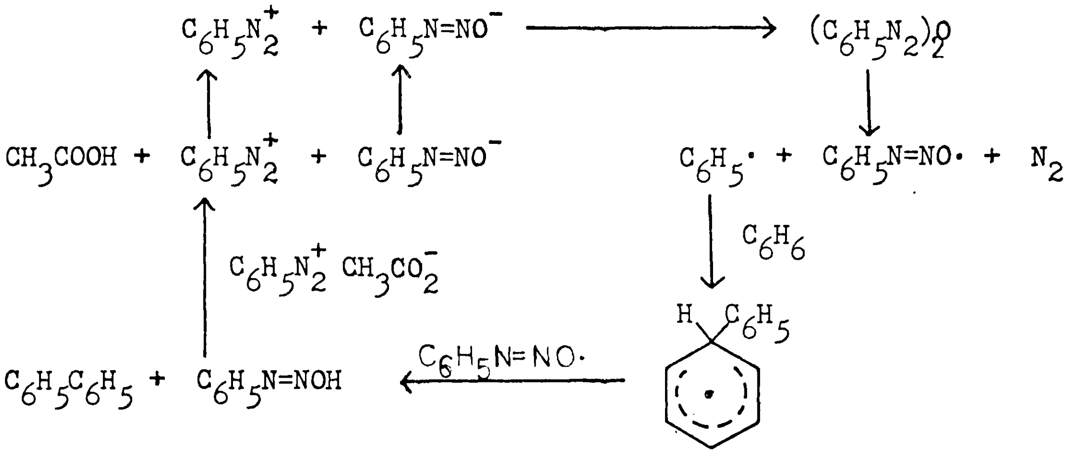
Another satisfactory feature of the mechanism was the postulate of the formation of acetic acid by a chain process from acetate ions and not from the unstable acetyloxy radical. The proposed mechanism involves a chain reaction initiated by acetate ion attack on benzenediazo acetate, thus leading to the requirement that trace amounts, only, of acetic anhydride should be formed.

$$C_6H_5N(NO)CO.CH_3 \longrightarrow C_6H_5N{=}NO.CO.CH_3 \rightleftharpoons C_6H_5N_2^+CH_3CO_2^-$$

Initiation:

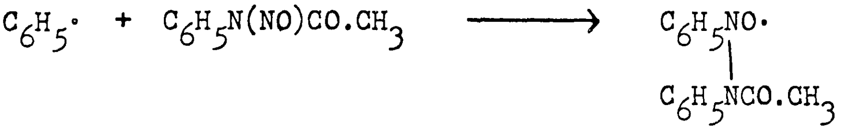
$$C_6H_5N{=}NO.CO.CH_3 + CH_3COO_2^- \longrightarrow C_6H_5N{=}NO^- + (CH_3CO)_2O$$

Chain Process :



Scheme 2.

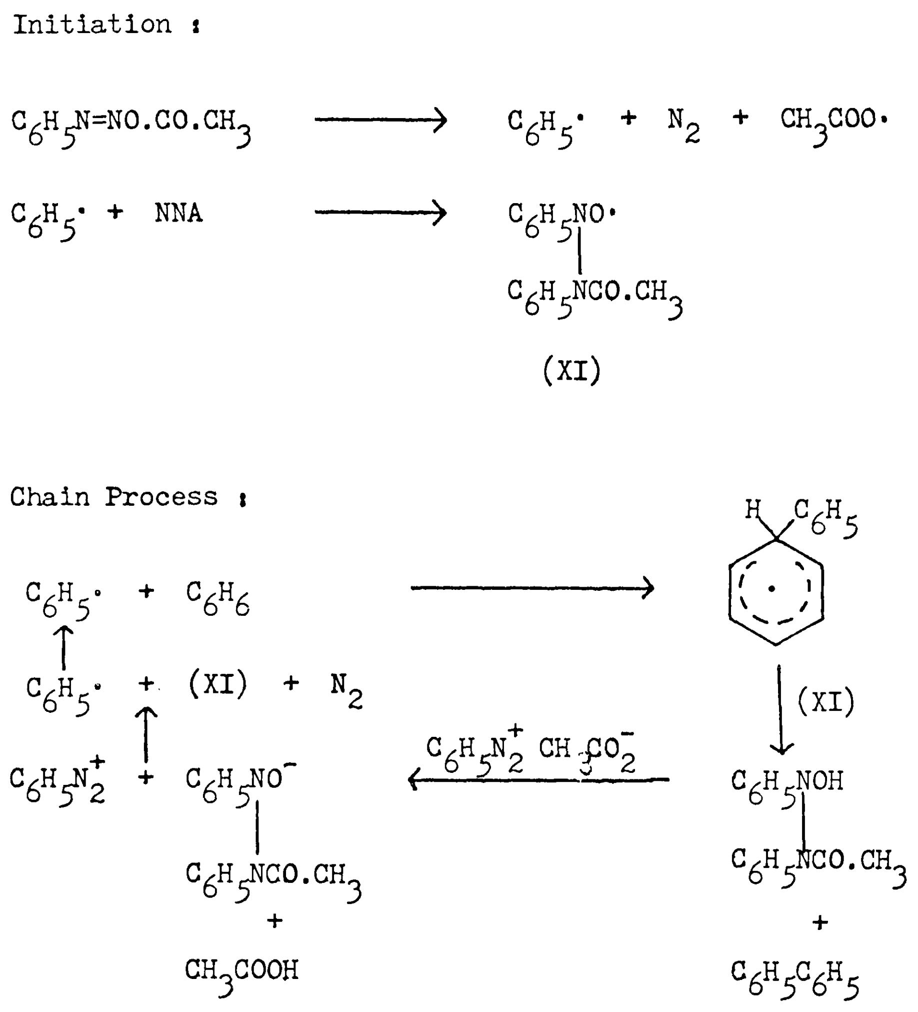
Ruchardt et al.[98,99] supported this mechanism with the observation of a long-lived ESR signal which they attributed to the PhN=NO· radical. This ESR signal was later identified, however, as due to (N-phenylacetamido)phenylnitroxide (PAPN) (XI)[100,101], produced by scavenging of a phenyl radical by N-nitroacetanilide (NNA), reaction (56).



$$C_6H_5\cdot \;+\; C_6H_5N(NO)CO.CH_3 \longrightarrow \begin{array}{c} C_6H_5NO\cdot \\ | \\ C_6H_5NCO.CH_3 \end{array} \qquad (56)$$

(XI)

On the strength of this Chalfont and Perkins[100] proposed a new chain mechanism for the decomposition of N-nitrosoacetanilide in benzene based on the stable PAPN radical (XI) as the chain-propagating and oxidising radical (scheme 3).



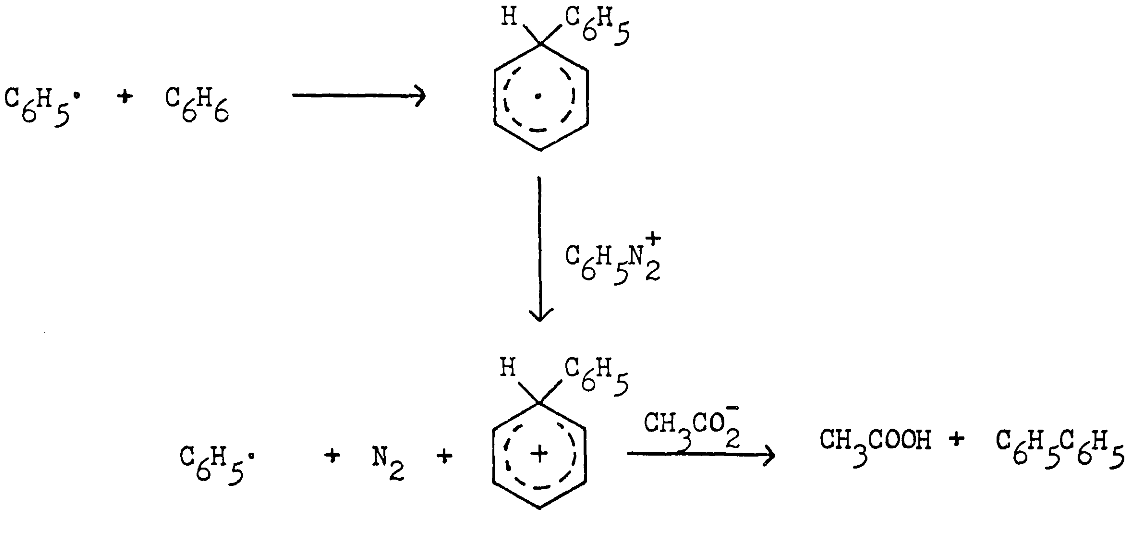
Scheme 3.

Subsequent ESR work by Cadogan et al.[102] has reconciled the apparently conflicting views expressed in schemes 2 and 3. These workers have shown that decomposition of N-nitrosoacetanilide, in organic solvents, leads to a second ESR signal which they have attributed to the phenyldiazoxyl radical (as in scheme 2) with the difference that this is a σ-radical rather than a π-radical as thought by Ruchardt et al.[98]

Cadogan et al.[102] also observed that this signal, attributable to PAPN (XI), unlike that of σ-PhN=NO·, is not present in all solvents. The constancy of the appearance of σ-PhN=NO·, regardless of solvent, led these workers to favour the Ruchardt and Freudenberg Scheme (2), as the usual product-forming sequence, although in those cases where both signals appear (e.g. with benzene as solvent) they pointed out that both schemes might be operative. Cadogan _et al._[102], however, favour a simpler chain propagation once initiation via scheme 2 or, in some circumstances scheme 3, has taken place, involving a redox reaction of the intermediate cyclohexadienyl radical with unchanged diazonium cation (scheme 4) leading to a phenyl radical, which continues the chain, and a phenylcyclohexadienyl cation, which reacts with acetate ion to give acetic acid and biphenyl. Direct evidence in support of this scheme has been provided by Nonhebel _et al._[29]

Initiation : $\longrightarrow$ $C_6H_5\cdot$ via schemes 2 and/or 3.

Chain Propagation :



Scheme 4.

Acylarylnitrosamines can also decompose by an ionic route to give arynes. Much research into this aspect of the chemistry of acylarylnitrosamines has been carried out, mainly by Cadogan and his co-workers[103-108], and this work has very recently been reviewed in detail by Cadogan.[109]

4.4 Phenylazotriphenylmethane

Phenylazotriphenylmethane (PAT) is another extensively studied source of phenyl radicals.[110-114] In aromatic solvents it decomposes at 60-80° to give products which include mainly triphenylmethane and biaryl together with some tetraphenylmethane.

The rate of decomposition is independent of the initial concentration of PAT and follows first-order kinetics.[115] Kinetic studies have established that no chain mechanism occurs.[115-119] The homolysis was originally rationalised in terms of a concerted two-bond cleavage[115];

$$\mathrm{Ph.N{:}N.CPh_3} \longrightarrow \mathrm{Ph\cdot} + \mathrm{N_2} + \mathrm{\cdot CPh_3} \qquad (57)$$

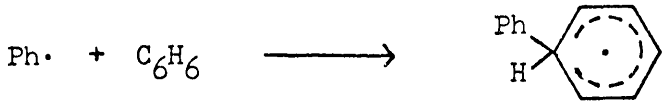
A step-wise homolysis was later suggested[119] in which the first stage is rate determining,

$$\mathrm{Ph.N{:}N.CPh_3} \xrightarrow{\text{slow}} \mathrm{Ph.N{:}N\cdot} + \mathrm{\cdot CPh_3} \qquad (58)$$

$$\mathrm{Ph.N{:}N\cdot} \xrightarrow{\text{fast}} \mathrm{Ph\cdot} + \mathrm{N_2} \qquad (59)$$

the second stage being very rapid since nitrogen evolution is quantitative, and also the rate of decomposition is not suppressed by the presence of added triphenylmethyl.[120] Viscosity studies by Pryor and Smith[121], and CIDNP studies by Garst and Siefert[122], have substantiated this proposal.

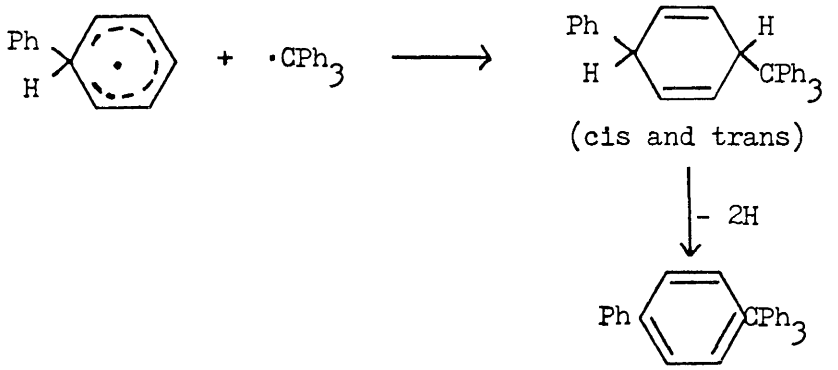
A suggestion[95] was made that free phenyl radicals are not formed in this reaction. This view was supported by the absence (a) of dihydrobiphenyls and tetrahydroquaterphenyls, and (b) of isotope effects. It was thus concluded that phenylation occurred by the rapid formation of the phenylcyclohexadienyl radical (60) and its subsequent rapid dehydrogenation (61) by triphenylmethyl radicals, all within a solvent cage :



(60)

(61)

However, products of a radical-coupling process (62) have been isolated from the reaction of PAT in benzene.[123,124] This reaction was shown to proceed via free radical intermediates of sufficient lifetime to permit escape from a solvent cage by the isolation of all

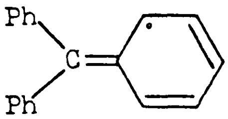


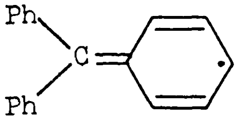
(62)

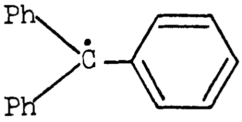
possible 'crossed' products from the decomposition of a mixture of two appropriately substituted arylazotriarylmethanes. Since the hydrogen transfer reaction (61) parallels reaction (62), by extension it must also involve free radicals.[123,124] Studies by Garst and

Cole[125] of (a) the effect of scavengers iodine and carbontetrabromide, and (b) the amount of benzene produced when PAT is decomposed in toluene and chlorobenzene, supports the *free* radical interpretation, as does work by Russell and Bridger[126] on the decomposition of PAT in a number of solvent combinations.

It has been suggested[124] that the failure to observe dihydrobiphenyls and tetrahydroquaterphenyls in the reaction of PAT in aromatic solvents might be due to a build-up in stationary-state concentration of the resonance stabilised $\cdot CPh_3$ radical (XII-VIV) which acts as a radical trap.


(XII)

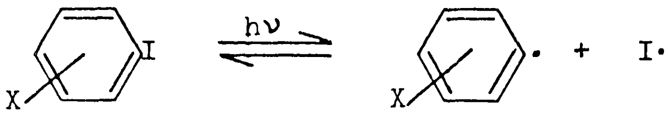

(XIII)


(XIV)

This radical is believed to lead to other anomalies in phenylation reactions of PAT compared to those of other phenyl radical initiators. For example, with nitrobenzene, very low yields of the nitrophenyls are observed[127] as a result of the tendency of the triphenylmethyl radical to react with the nitro-group. The phenylation of pyridine gives abnormal isomer distribution for the phenylpyridines[128] due to the removal of some of the 2-phenylpyridine by the triphenylmethyl radical to produce 2-phenyl-5-tritylpyridine.[129] More recently abnormal isomer distributions have also been observed for the chlorobiphenyls[27] formed by the decomposition of PAT in chlorobenzene due to the formation of trans-1-chloro-2-phenyl-4-trityl-2,4-dihydrophenyl almost entirely at the expense of *o*-chlorobiphenyl.

4.5 Photochemical and Radiochemical Methods

Photochemical methods have been explored as potential processes for homolytic arylation.[130-133] The most well known involves the photolysis of aryl iodides (63).[132,133] Since it is usually a 'clean' reaction with high yields of biaryl being formed and an almost quantitative release of iodine, it has been developed as a useful process in the preparation of biaryls.[132,133]



(63)

Radiolysis of certain aromatic compounds is also a potential source of aryl radicals, and γ-radiolysis of bromobenzene has been shown to give phenyl radicals which can effect phenylation of the bromobenzene.[134] Radiolysis of biphenyl has been shown to give isomeric quaterphenyls[135,136]

4.6 Miscellaneous Methods

Aryl radicals have been shown to be formed, and to effect arylation of the substrate at high temperatures, by the pyrolysis of aromatic halides.[137,138] In the gas phase aryl radicals can be formed by the pyrolysis (600°) of aromatic nitro-compounds[139], this method having recently been reviewed.[140] The formation of aryl radicals from aryl halides in the presence of Griegnard reagents and transition-metal halides has been reported.[141,142]

I. 5 Partial Rate Factors: Monosubstituted Benzenes

With respect to a monosubstitited benzene (PhX) the partial rate factor (F_r) is an expression of the reactivity of any one position in PhX with reference to that of any one position in benzene. The measurement of partial rate factors involves the determination of (a) the ratio of the total rate of substitution in PhX to that in benzene ($^{PhX}_{PhH}K$), and (b) the proportions (ν, μ, π, respectively) in which the o-, m-, and p- isomers are formed by the substitution of PhX. The partial rate factors for the three positions are then given by eqns. (64)-(66).

$$F_o = 3\nu\,^{PhX}_{PhH}K \qquad (64)$$

$$F_m = 3\mu\,^{PhX}_{PhH}K \qquad (65)$$

$$F_p = 6\pi\,^{PhX}_{PhH}K \qquad (66)$$

The method used for the determination of the total rate ratios is based on the principle of competition between two substrates present in large excess. Using a third substrate PhY, the rate ratio $^{PhX}_{PhH}K$ may be obtained indirectly from the multiplication rule (67).

$$^{PhX}_{PhH}K = {}^{PhY}_{PhH}K \times {}^{PhX}_{PhY}K \qquad (67)$$

Partial rate factors for the phenylation of aromatic compounds with benzoyl peroxide have been determined by a number of workers.[127, 128,143-149] Some of the results for phenylation with benzoyl peroxide at 80° are summarised in Table (1). These results show that in the absence of steric factors all substituents activate the nucleus slightly towards attack by phenyl radicals, independant of their polar characteristics, but that the o-isomer is formed in the largest quantity. For compounds containing strongly activating groups the partial rate factors for the o- and p-positions are higher than that of the m-position, although with other substituents this activation is less apparent.

Table (1)

Relative rates and partial rate factors for the phenylation of aromatic compounds with benzoyl peroxide at 80°.

Substrates	Relative Rate (PhH = 1)	Isomer Ratio (%) o-	m-	p-	Partial Rate Factors F_o	F_m	F_p
$PhNO_2$	2.94	62.5	9.8	27.7	5.5	0.86	4.9
PhF	1.03	55.2	29.8	15.0	1.7	0.92	0.93
PhCl	1.06	56.9	25.6	17.5	1.8	0.81	1.1
PhBr	1.29	55.7	28.8	15.5	2.2	1.1	1.2
PhI	1.32	51.7	31.6	16.7	2.0	1.3	1.3
PhMe	1.23	65.4	20.0	14.6	2.4	0.74	1.1
PhEt	0.90	51.0	28.0	21.0	1.4	0.76	1.1
$PhPr^i$	0.64	30.0	42.0	28.0	0.58	0.81	1.1
$PhBu^t$	0.64	24.0	49.0	27.0	0.46	0.94	1.0
PhPh	2.94	48.5	23.0	28.5	2.1	1.0	2.5
PhCN	3.7	60.0	10.0	30.0	6.5	1.1	6.1
$PhCO_2Me$	1.77	57.0	17.5	25.5	3.0	0.93	2.7
PhOMe	2.01	69.8	14.5	15.8	4.2	0.87	1.9
Pyridine	1.04	54.0	32.0	14.0	1.7	1.0	0.87

In the formulation of partial rate factors it is assumed that the rates and relative rates of formation of binuclear products ($Ar.C_6H_4X$) may be taken as the corresponding rates and relative rates of addition of the aryl radical to the various nuclear positions in the substrate PhX; i.e. in the formation of the various σ-complexes. If the σ-complexes are selectively diverted from direct oxidation to the biaryl by the processes of dimerisation and disproportionation then this fundamental assumption is no longer valid. On these grounds the validity of partial rate factors as true measures of the reactivity of the various positions in the aromatic nucleus have been criticised.[32,33,135] The observations (a) of a non-statistical hydrogen isotope distribution in the binuclear products (though not in the unconsumed substrate) in the phenylation of $[^2H]$ benzene indicating that the oxidation of the σ-complex to biphenyl must compete with side-reactions leading to non-biaryl formation, and (b) that these side-reactions can be largely suppressed, and the yields of biaryls considerably enhanced, by conducting the decomposition of benzoyl peroxide in a stream of oxygen, led Eliel _et al_.[24,44] also to criticise the assumption, and hence the validity of measured partial rate factors.

Further investigation of the influence of oxygen on phenylation reactions,[51] however, revealed that the diversion reactions of σ-complexes are non selective. It has also been shown[150] that neither variation in peroxide concentration, nor the inclusion of benzene as a co-reactant influences the relative rates and isomer distributions of the mono-substituted benzenes. Qualitative results reported by Morrison _et al_.[51] are given in Table (2). Partial rate factors calculated for reactions in either the presence or absence of other additives have shown no variation.[60,151]

Table (2)

Reactions of aromatic substrates with benzoyl peroxide in the presence and absence of oxygen (80°).

Substrate	Oxygen	Yield of Biaryl (mole per mole peroxide)	Isomer Distribution % o-	m-	p-	Total Rate Factor (PhH=1)
PhOMe	-	0.50	69.8	14.7	15.6	1.99
PhOMe	+	1.35	69.8	14.5	15.8	2.01
PhBr	-	0.33	56.2	27.3	16.5	1.14
PhBr	+	1.58	55.2	28.8	16.0	1.11
$PhBu^t$	-	0.72	21.2	49.9	29.0	0.63
$PhBu^t$	+	1.40	21.2	50.0	28.8	0.61
$PhNO_2$	-	0.19	63.2	9.7	27.1	2.95
$PhNO_2$	+	0.68	62.8	9.7	25.7	2.85

Recently, the question of the validity of partial rate factors has been raised again by Norman[152] and by Bonnier.[153-155] Norman[152] noted that the isomer ratio and total rate factors in the decomposition of benzoyl peroxide in anisole are not the same in the presence and absence of cupric benzoate. Bonnier et al.[153] found that the isomer ratio of the phenylation products of 4-methylpyridine depends on the concentration of the peroxide, although no change is observed when additives, such as oxygen and nitrobenzene, are present. These workers also reported an isotope effect in the phenylation of deuterated 4-methylpyridine.[154] These observations were held to show that the side-reactions of the various σ-complexes could be selective.

In comfirmation, the isomer ratios and partial rate factors in the phenylation of pyridinium chloride were reported[156] to change drastically in the presence of catalytic amounts of nitrobenzene.

Partial rate factors for many solvents have been determined from the multiplication rule, by competitive reactions using nitrobenzene as the standard solvent. Recently, Ohta and Toumara[157] have pointed out, however, that nitrobenzene is not suitable when the competing substrate contains abstractable hydrogen atoms because the intermediate nitrophenylcyclohexadienyl radical is diverted to products other than nitrobiphenyls.

Davies, Hey and Summers[158] embarked on a study of partial rate factors using p-dichlorobenzene as the standard solvent in competitive reactions. They found that the total and partial rate factors were of the same order but slightly higher than the values obtained for mono-substituted benzenes using nitrobenzene as standard solvent except in the case of toluene, when, with p-dichlorobenzene significantly higher values were obtained. This substantiated the observation[154] that the nitrophenylcyclohexadienyl radical reacts with the side-chain, suppressing the normally complicating reaction of the phenyl radical with the side-chain in toluene, leading to the formation of bibenzyl.[20]

In the early studies, benzene was not considered to be a suitable standard for competitive experiments because of ready loss of the relatively volatile biphenyl in the work up. Recently, using new techniques, this problem has been solved[159,160] and partial rate factors have been redetermined (a) using benzene in competitive reactions with the monosubstituted aromatic solvent, and (b) having an additive present. The additive chosen was the one found to be the most efficient in giving near-quantitative conversion of the σ-complex to biaryl. In most cases ferric benzoate was found to be most efficient.

The partial rate factors obtained,[161] although differing slightly from earlier results (possibly due to higher yields of biaryls), were of the same relative order. This was held to show that the conclusions reached in the earlier work were still valid. The results also show that no complex formation between the arenes and the radicals of their precursors takes place in these competitive phenylation reactions. This complex formation has been suggested as a possible cause of discrepancies in the partial rate factors for the pentafluorophenylation of arenes[162] and the phenylation of polyfluoroarenes[163] (see section I. 6.4).

I. 6. Homolytic Arylation of Polyfluoroaromatic Compounds

6.1 Introduction

The first reported free-radical reaction involving polyfluoroaromatic compounds was the addition of chlorine, under ultraviolet irradiation, to hexafluorobenzene and pentafluorobenzene to give hexachlorohexafluorocyclohexane and hexachloropentafluorocyclohexane, respectively.[164,165] Homolytic attack on the nucleus of hexafluorobenzene by trichlorosilyl radicals has also been demonstrated.[166] The best documented and most studied homolytic substitution reaction is, however, arylation, and this is also the case in the polyfluoroaromatic series.

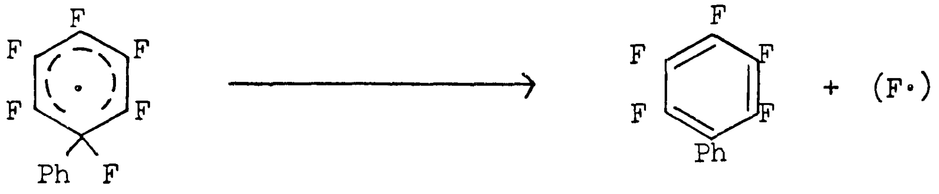
The most comprehensive study is of the homolytic arylation of hexafluorobenzene, which would be expected to involve quite different energetic considerations to those of benzene itself. Specifically, a stronger bond is being broken (C-F) and a different atom (F•) is being displaced. These processes have been found to influence the mechanism of the homolytic arylation reaction of hexafluorobenzene.

6.2 Hexafluorobenzene

The homolytic arylation of hexafluorobenzene with phenyl radicals derived form benzoyl peroxide was first reported by Claret, Coulson and Williams.[167] These workers found that this reaction gave good yields of 2,3,4,5,6-pentafluorobiphenyl, together with small amounts of benzene, benzoic acid and hydrogen fluoride, and some high boiling residue.[168] Subsequent work[169-172] has substantiated these findings and also revealed the existence of small amounts of 2,2',3,4,5,6-hexafluorobiphenyl from this reaction.

The major products from the decomposition of benzoyl peroxide in hexafluorobenzene parallel those found in the benzene system. A kinetic study of this reaction[172,173] has shown that it proceeds by a spontaneous first-order process accompanied by an induced 1.5 order process. The mechanism for the decomposition of benzoyl peroxide in hexafluorobenzene might, thus, appear to be analogous to that for benzene. Problems arise, however, when the defluorination of the intermediate σ-complex is considered.

The yield of the pentafluorobiphenyl depends on the conditions of distillation required for separation of the biaryl from the product mixture.[174,175] It is increased at elevated temperatures, indicating that some of the pentafluorobiphenyl is formed by pyrolysis of the polynuclear residue. The majority of the pentafluorobiphenyl produced from the decomposition must, however, come from the direct defluorination of the intermediate σ-complex.



(68)

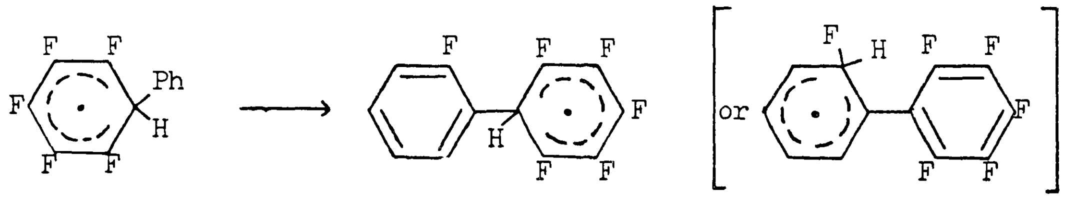
($\sigma_{F\cdot}$)

The C-F bond is a strong bond and would not be expected to undergo homolysis to form either <u>free</u> fluorine atoms or fluorine molecules, since both of these processes are strongly endothermic. The defluorination of $\sigma_{F\cdot}$ might be considered to be effected by benzoyloxy radicals or benzoyl peroxide itself [eqn. (69)], an analogy with the benzene system [eqns. (21) and (23)] which is confirmed by the kinetic form. This reaction, however is endothermic and, therefore, unsatisfactory as an

$$\sigma_{F\cdot} + BzO\cdot\ (Bz_2O_2) \longrightarrow PhC_6F_5 + BzOF\ (BzO\cdot) \qquad (69)$$

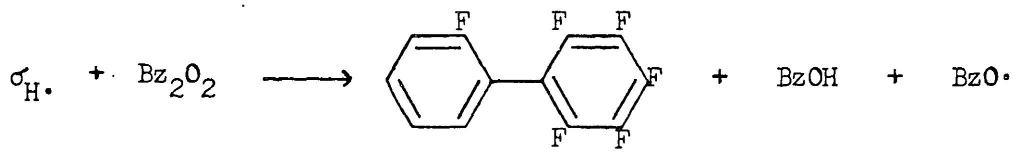
explanation of the formation of high yields of pentafluorobiphenyl.

The small amounts of 2,2',3,4,5,6-hexafluorobiphenyl formed in this reaction may be accounted for by the rearrangement of $\sigma_{F\cdot}$ to $\sigma_{H\cdot}$ [eqn. (70)] with subsequent dehydration of the latter [eqn. (71)].[171]



(70)

($\sigma_{F\cdot}$) ($\sigma_{H\cdot}$)



$\sigma_{H\cdot}$ + Bz_2O_2 ⟶ + BzOH + BzO· (71)

This rearrangement of $\sigma_{F\cdot}$ seems to involve a greater activation energy than its aromatisation through defluorination, since (a) the yield of 2,2',3,4,5,6-hexafluorobiphenyl is much lower than that of pentafluorobiphenyl at 80°, and (b) the decomposition of nitrobenzene at 600° in hexafluorobenzene gives similar yields of pentafluorobiphenyl and 2,2',3,4,5,6-hexafluorobiphenyl.[169] The only comparable rearrangement involves hydrogen and deuterium.[176] Exchange occurs readily in this system as would be expected, since hydrogen and deuterium atoms have more nearly the same bond strengths and mobility than hydrogen and fluorine atoms.

An insight into the mechanism of defluorination of the $\sigma_{F\cdot}$ to yield pentafluorobiphenyl was given by Bolton and Sandall.[177] These workers found that on addition of p-fluorobenzoic acid to the benzoyl peroxide-hexafluorobenzene system, the yield of 2,3,4,5,6-fluorobiphenyl increased at the expense of both 2,2',3,4,5,6-hexafluorobiphenyl and the radical combination products. Furthermore, the increased yield of pentafluorobiphenyl was accompanied by the formation of 2,3,4,4',5,6-hexafluorobiphenyl in amounts approximately proportional to the amount of acid added, and by the increased production of hydrogen fluoride. From these results scheme (72-74) was suggested to account for the formation of pentafluorobiphenyl and 2,3,4,4',5,6-hexafluorobiphenyl. An analogous sequence is possible using benzoic acid, which is formed during the arylation of hexafluorobenzene by benzoyl peroxide. It has thus been suggested[178] that this benzoic acid is the essential source of hydrogen in the defluorination of the intermediate $\sigma_{F\cdot}$ radical. This suggestion has been supported by a study of the decomposition of phenylazotriphenylmethane (PAT) in hexafluorobenzene (80°).[179] Very little pentafluorobiphenyl was found in this reaction

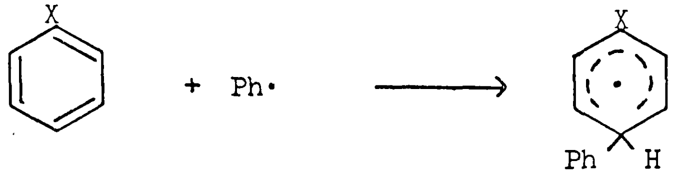
$$\sigma_{F\cdot} + \underline{p}\text{-F.}C_6H_4\text{.COOH} \longrightarrow PhC_6F_5 + HF + \underline{p}\text{-F.}C_6H_4\text{.COO}\cdot \qquad (72)$$

$$\underline{p}\text{-F.}C_6H_4\text{.COO}\cdot \longrightarrow \underline{p}\text{-F.}C_6H_4\cdot + CO_2 \qquad (73)$$

$$\underline{p}\text{-F.}C_6H_4\cdot + C_6F_6 \xrightarrow[\text{analogous steps}]{\text{several}} \underline{p}\text{-F.}C_6H_4\text{.}C_6F_5 \qquad (74)$$

until a suitable hydrogen donor was added.

Benzoic acid may be formed initially, either through phenylation of benzoyl peroxide (75-77) or from rearrangement of the $\sigma_F\cdot$ radical to form 2,2',3,4,5,6-hexafluorobiphenyl [eqns. (70) and (71)], but the amount obtained from these reactions would be insufficient to account for the high yields of pentafluorobiphenyl observed. It was mentioned earlier [eqn. (69)] that defluorination of $\sigma_F\cdot$ by benzoyloxy radicals or benzoyl peroxide would not be expected. It is still possible, however, for an addition reaction to occur between $\sigma_F\cdot$ and either of these species [eqn. (78)].



(75)

(XV)

$$\text{(XV)} + \text{BzO}\cdot\ (\text{Bz}_2\text{O}_2) \longrightarrow \text{BzOH} + \text{Ph.PhX}\ (+\ \text{BzO}\cdot) \qquad (76)$$

$$\text{Ph.PhX} \longrightarrow \text{Ph.C}_6\text{H}_4\text{.COO}\cdot + \text{BzO}\cdot \qquad (77)$$

(X = BzO.O.CO)

$$\sigma_F\cdot + \text{BzO}\cdot\ (\text{Bz}_2\text{O}_2) \longrightarrow \sigma_F\text{-OBz}\ (+\text{BzO}\cdot) \qquad (78)$$

The tertiary esters formed in this reaction can undergo transesterification by HF [eqn. (79)], providing a route for the recycling of a limited supply of benzoic acid through the reaction.

$$\sigma_F\text{-OBz} + \text{HF} \longrightarrow \sigma_F\text{F} + \text{BzOH} \qquad (79)$$

A mechanism has been proposed[178,180] to account for the observed products and kinetics of the reaction of benzoyl peroxide in hexafluorobenzene. The initiation reaction (80) is known to be involved in all homolytic reactions with benzoyl peroxide as phenyl radical precursor.

$$\mathrm{Bz_2O_2} \xrightarrow{\text{slow}} 2\ \mathrm{BzO}\cdot \tag{80}$$

$$\mathrm{BzO}\cdot \longrightarrow \mathrm{Ph}\cdot + \mathrm{CO_2} \tag{81}$$

$$\mathrm{Ph}\cdot + \mathrm{C_6F_6} \longrightarrow [\mathrm{PhC_6F_6}]\cdot = (\sigma_F.) \tag{82}$$

$$\mathrm{BzO}\cdot + \mathrm{C_6F_6} \longrightarrow [\mathrm{BzO.C_6F_6}]\cdot = (\sigma'_F.) \tag{83}$$

$$\sigma_F. \longrightarrow \sigma_H. \tag{84}$$

$$\sigma_H. + \mathrm{Bz_2O_2} \xrightarrow{\text{slow}} 2'\text{-}\mathrm{F.Ph.C_6F_5} + \mathrm{BzOH} + \mathrm{BzO}\cdot \tag{85}$$

$$\sigma_F. + \mathrm{Bz_2O_2} \xrightarrow{\text{slow}} \sigma_F\text{-}\mathrm{OBz} + \mathrm{BzO}\cdot \tag{86}$$

$$\sigma'_F. + \mathrm{Bz_2O_2} \xrightarrow{\text{slow}} \sigma'_F\text{-}\mathrm{OBz} + \mathrm{BzO}\cdot \tag{87}$$

$$2\ \sigma_F.\ (2\sigma'_F.) \longrightarrow (\sigma_F)_2\ [(\sigma'_F)_2] \tag{88}$$

$$\sigma_F.\ (\sigma'_F.) + \mathrm{Ph}\cdot \longrightarrow \sigma_F\text{-}\mathrm{Ph}\ (\sigma'_F\text{-}\mathrm{Ph}) \tag{89}$$

$$\sigma_F.\ (\sigma'_F.) + \mathrm{BzO}\cdot \longrightarrow \sigma_F\text{-}\mathrm{OBz}\ (\sigma'_F\text{-}\mathrm{OBz}) \tag{90}$$

$$\sigma_H. + \mathrm{BzO}\cdot \longrightarrow 2'\text{-}\mathrm{F.C_6H_4.C_6F_5} + \mathrm{BzOH} \tag{91}$$

$$\sigma_F. + \mathrm{BzOH} \longrightarrow \mathrm{PhC_6F_5} + \mathrm{HF} + \mathrm{BzO}\cdot \tag{92}$$

$$\mathrm{Ph}\cdot + \mathrm{BzOH} \longrightarrow \mathrm{PhH} + \mathrm{BzO}\cdot \tag{93}$$

$$\mathrm{R_F\text{-}OBz} + \mathrm{HF} \longrightarrow \mathrm{R_FF} + \mathrm{BzOH} \tag{94}$$

The subsequent addition of radicals to the substrate is similarly proposed by analogy with aromatic hydrocarbon systems. The main driving force here, as with other aromatic systems, is the delocalisation of the unpaired electron over the cyclohexadienyl system to form a more stable radical. The rearrangement (84), unusual as it is, seems the simplest explanation of both the 2,2',3,4,5,6-hexafluorobiphenyl formed in the reaction and the maintenance of an induced decomposition of kinetic order 1.5, in conjunction with reactions (85)-(87). The idea of a simple aromatic substitution process by some precursor of hydrogen fluoride has been rejected[173] since only the *o*-atom is attacked; no 2,3,3',4,5,6- or 2,3,4,4',5,6-hexafluorobiphenyl has been detected although homolytic fluorination of the initially-formed pentafluorobiphenyl would be expected to give all three possible isomers.

The termination processes (88) are those required for the kinetic form involving 1.5 order induced decomposition of the peroxide. Such termination reactions are not required exclusively; they need only represent the majority of termination processes for that section of the reaction proceeding by the induced mechanism. However, since this mechanism involves the formation of benzoyloxy radicals , which subsequently give phenyl radicals and hence biaryl products, it is unlikely that one specific termination sequence is unique to a particular part of the reaction and thus, reactions (89)-(91) are not excluded as minor contributors.

Disproportionation (95) has been discounted[173,178] as a possible

$$2\ \sigma_F\cdot \longrightarrow PhC_6F_5 + PhC_6F_7 \qquad (95)$$

termination reaction since this reaction requires the abstraction of fluorine in a radical-radical encounter in competition with the much more favourable radical-radical combination reaction (88).

The defluorination step (92) is important since it allows the formation of pentafluorobiphenyl by an energetically feasible route and it provides an additional route for regeneration of benzoyloxy radicals. The abstraction of hydrogen from benzoic acid need not be unique to the σ-intermediate; other radicals which exist in the solution may similarly be capable of doing so. The candidates for consideration in this context are the benzoyloxy radicals and phenyl radicals:

$$BzO\cdot + BzOH \longrightarrow BzOH + BzO\cdot \qquad (96)$$

$$Ph\cdot + BzOH \longrightarrow PhH + BzO\cdot \qquad (97)$$

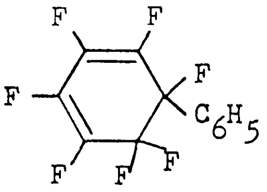
The reaction with benzoyloxy radicals is a simple exchange unless a foreign aroic acid is added. The reaction with phenyl radicals gives benzene, which has been observed as a reaction product.[168] With substituted aroyl peroxides the substituted benzenes have also been found.

A σ-complex might be expected to be formed by the reaction of benzoyloxy radicals with the solvent (83), by analogy with the benzene system. If this is the case, it would be expected that this $\sigma'_{F}\cdot$ radical would also be defluorinated by reaction with benzoic acid (98). The expected product, pentafluorophenyl benzoate, has not been isolated, and

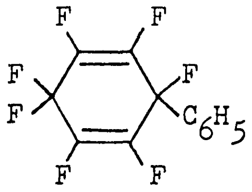
$$[BzO.C_6F_6]\cdot \; + \; BzOH \longrightarrow C_6H_5CO.O.C_6F_5 \; + \; BzO\cdot \; + \; HF \qquad (98)$$

therefore, if $\sigma'_{F}\cdot$ is formed at all, it does not lose fluorine.

The transesterification reaction [eqn. (78)] postulated for the recycling of benzoic acid, need not be limited to tertiary esters produced by reaction of $\sigma_{F}\cdot$ with benzoyloxy radicals or with benzoyl peroxide. Other esters may be formed and, thus, $R_{F}F$ [eqn. (94)] could also be a species such as $\sigma'_{F}F$ and $2\sigma_{F}F$ etc... The species σ_{F}–OBz would, however, be expected to be the most abundant tertiary ester in the benzoyl peroxide-hexafluorobenzene system. Transesterification of this is predicted to give,[173] as well as benzoic acid, isomeric heptafluorodihydrobiphenyls, products considered not to be formed by disproportionation.[175,178] These derivatives of dihydrobiphenyl have now been identified[181] in the reaction of benzoyl peroxide with hexafluorobenzene and with octafluorotoluene. The structure of such derivatives of dihydrobiphenyl is still uncertain. The parent compound, Ph.C_6F_7, may be either 1,2-dihydro-1,2,2,3,4,5,6-heptafluorobiphenyl (XVI) or 1,4-dihydro-1,2,3,4,4,5,6-heptafluorobiphenyl (XVII).



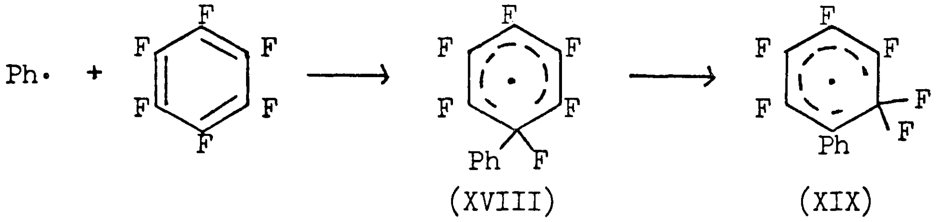
(XVI)



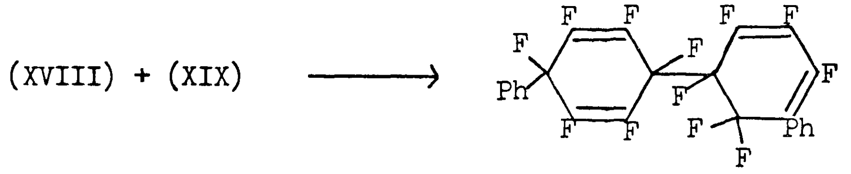
(XVII)

Kobrina *et al.*[175] reported that dehalogenation of the residue of the reaction of benzoyl peroxide with hexafluorobenzene gives 2,4'-, 4,4'- and 3,4'- quaterphenyl derivatives. The last structure, which cannot arise from dimerization of $\sigma_{F\cdot}$, was thought to arise from 1,2-migration of a fluorine atom in the intermediate [reactions (99) and (100)].

Williams *et al.*[181] proposed that $\sigma_{F\cdot}$ might react with the dihydrobiphenyl derivatives (XVI) and (XVII) to give radicals containing the 2,4'-, 3,4'- or 4,4'-quaterphenyl skeleton. Both benzoic acid and the benzoyloxy radical are expected to give trapping products from radicals which could, in turn, give polyfluoroderivatives of 2,4'-, 3,4' and 4,4'-quaterphenyl, upon treatment with zinc dust; i.e. Kobrina's conditions for dehalogenation. The formation of 3,4'-*bis*-(phenyl)-octafluorobiphenyl from reactions of (XVI) is shown in eqns. (101)-(103). The analogous derivatives of 2,4'- and 4,4'-*bis*-(phenyl)-octafluorobiphenyl may similarly be obtained.

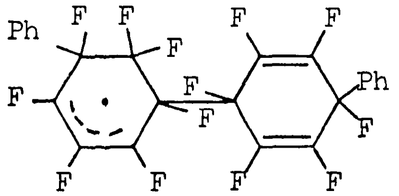


(99)



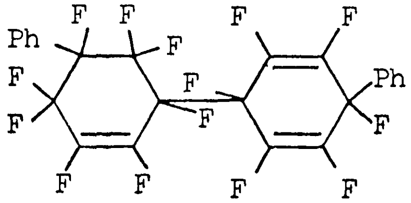
(100)

$$(XVI) + \sigma_{F}\cdot \longrightarrow \qquad (101)$$



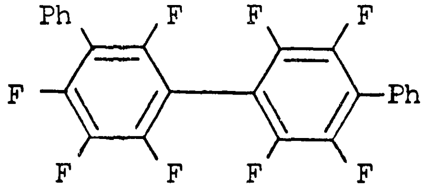
(XX)

$$(XX) \xrightarrow[HF]{BzO\cdot} \qquad (102)$$



(XXI)

$$(XXI) \xrightarrow{Zn\ dust} \qquad (103)$$



In the benzoyl peroxide-benzene system the terphenyls observed were considered to arise from subsequent arylation of biaryl (Section I. 2.1).[36] Terphenyls have now been observed in the hexafluorobenzene system.[181] These could arise (a) from subsequent arylation of the biaryl [eqn. (104)], (b) from radical-radical combinations [eqn. (105)], or (c) from the arylation of benzoyl peroxide or benzoic acid [eqn. (106)], leading to a biphenylyl radical which could subsequently undergo reactions parrallel to those of the aryl radical [eqns. (107)-(109)]. Evidence of the biphenylyl radical[181] suggests that arylation of the benzoyl peroxide or benzoic acid [reactions (107)-(109)] is the true path for the formation of the observed terphenyls.

$$C_6F_5C_6H_5 + C_6H_5\cdot \longrightarrow C_6F_5\cdot C_6H_4\cdot C_6H_5 + C_6H_5\cdot C_6F_4\cdot C_6H_5 \qquad (104)$$

$$[C_6H_5\cdot C_6F_6]\cdot + C_6H_5\cdot \longrightarrow C_6H_5\cdot C_6F_6\cdot C_6H_5 \qquad (105)$$

$$C_6H_5\cdot + (C_6H_5COO)_2 \longrightarrow C_6H_5\cdot C_6H_4\cdot COO.OCOC_6H_5 \qquad (106)$$

$$C_6H_5\cdot C_6H_4\cdot COO.OCOC_6H_5 \longrightarrow C_6H_5\cdot C_6H_4\cdot COO\cdot \longrightarrow C_6H_5\cdot C_6H_4\cdot \qquad (107)$$

$$C_6H_5\cdot C_6H_4\cdot + C_6F_6 \longrightarrow [C_6H_5\cdot C_6H_4\cdot C_6F_6]\cdot \qquad (108)$$

$$[C_6H_5\cdot C_6H_4\cdot C_6F_6]\cdot \xrightarrow{[-F\cdot]} C_6H_5\cdot C_6H_4\cdot C_6F_5 \qquad (109)$$

6.3 Polyfluorobenzenes

From the studies of homolytic arylation of benzene and of hexafluorobenzene during the decomposition of benzoyl peroxide in these solvents, it has now been established that aryldehydrogenation and aryldefluorination proceed by seperate routes. In the intermediate polyfluorobenzenes both routes would be expected to occur. Wilson[182] investigated the thermal decomposition of benzoyl peroxide in pentafluorobenzene and in 1,2,4,5-tetrafluorobenzene and found that phenyldefluorination predominated in the reaction with pentafluorobenzene, whilst in the 1,2,4,5-tetrafluorobenzene system phenyldehydrogenation was predominant. More recently a comprehensive study of the thermal decomposition of benzoyl peroxide in a range of polyfluorobenzenes has been carried out.[163,183] The results of this study are given in Table (3). Phenyldefluorination appears to predominate in the 1,2,3,4-tetrafluorobenzene and pentafluorobenzene systems only because they have more fluorine-bearing sites that can be attacked. Even in the case of pentafluorobenzene, where the 3- and 6-positions are approximately equally affected by the other fluorine substituents

Table (3)

Molar Yields of Polyfluorobiphenyls from the thermolysis of Benzoyl Peroxide in Polyfluorobenzenes

Polyfluorobenzene	Polyfluorobiphenyl	Yield*	Isomer Ratio	
			Exp.	Calc.**
Fluorobenzene	2-Fluorobiphenyl	47.7	50	50
	3-Fluorobiphenyl	34.4	36	36
	4-Fluorobiphenyl	13.3	14	14
1,2-Difluorobenzene	2-Fluorobiphenyl	9.1	13	13
	2,3-Difluorobiphenyl	42.5	60	56
	3,4-Difluorobiphenyl	19.1	27	31
1,3-Difluorobenzene	3-Fluorobiphenyl	4.7	7	8
	2,4-Difluorobiphenyl	25.5	38	39
	2,6-Difluorobiphenyl	23.3	35	35
	3,5-Difluorobiphenyl	16.6	20	24
1,4-Difluorobenzene	2,5-Difluorobiphenyl	58.0	100	94
1,2,4-Trifluorobenzene	2,4-Difluorobiphenyl	3.7	6	5
	2,5-Difluorobiphenyl	3.7	7	6
	3,4-Difluorobiphenyl	<3	<5	4
	2,3,5-Trifluorobiphenyl	16.1	27	27
	2,4,5-Trifluorobiphenyl	12.1	20	21
	2,3,6-Trifluorobiphenyl	20.5	34	37
1,3,5-Trifluorobenzene	3,5-Difluorobiphenyl	<2	<8	13
	2,4,6-Trifluorobiphenyl	22.0	92	87
1,2,3,4-Tetrafluorobenzene	2,3,4-Trifluorobiphenyl	4.9	14	14
	2,3,6-Trifluorobiphenyl	13.9	54	61
	2,3,4,5-Tetrafluorobiphenyl	8.3	32	25
1,2,3,5-Tetrafluorobenzene	2,3,5-Trifluorobiphenyl	4.2	12	16
	2,4,6-Trifluorobiphenyl	10.8	32	9
	3,4,5-Trifluorobiphenyl	<0.7	<2	5
	2,3,4,6-Tetrafluorobiphenyl	18.2	54	72
1,2,4,5-Tetrafluorobenzene	2,4,5-Trifluorobiphenyl	15.0	26	21
	2,3,5,6-Tetrafluorobiphenyl	44.2	74	79

(*) (Moles of biaryl per mole of peroxide decomposed) x 100

(**) Using partial rate factors derived from arylation of fluorobenzene.[163]

(presupposing the effect of p-fluorine to be small, in keeping with the homolytic mechanisms[6]), hydrogen displacement proceeds with three times the ease of phenyldefluorination. However, phenyldefluorination is detectable even in the attack of some difluorobenzenes, although in small amount.

In the attack of simple arenes [Table (1)], o-attack is found to predominate, except in those cases, e.g. $PhBu^t$, where steric factors have an influence. This was thought to be due to the o-substituents stabilising the σ-intermediate. It can be seen, Table (3), that this o-attack is also predominant in the polyfluorobenzene systems.

6.4 Partial Rate Factors: Polyfluorobenzenes

The partial rate factors for the phenylation of chloro- and bromopentafluorobenzene with benzoyl peroxide by competition with benzene,[182] were reported by Williams[7]. The results are given in Table (4).

Table (4)

Phenylation of Chloro- and Bromo-Penatfluorobenzene (80°)

Substrate	Relative Rate (C_6F_6 = 1)	Isomer Distribution o-	m-	p-	Partial Rate Factors F_o	F_m	F_p
C_6F_5Cl	1.4	47.9	33.7	18.4	2.0	1.4	1.55
C_6F_5Br	1.0	45.2	37.4	17.4	1.4	1.1	1.05

These competition reactions involve the use of mixtures of benzene and a polyfluorobenzene. However, studies of heats of mixing,[184,185] phase diagrams,[186-188] and of refractive vapour pressure,[189] and dielectric and refractive index measurements,[190,191] have produced evidence that hexafluorobenzene forms complexes with benzene and other aromatic hydrocarbons. From crystallographic studies[192] on the solid phase it is known that hexafluorobenzene forms a 1:1 molecular complex with aromatic hydrocarbons. Their formation has been attributed to charge transfer with hexafluorobenzene acting as an electron donor. Although this complex formation decreases with less fluorinated benzene systems,[184] some evidence has been found for pentafluorobenzene-benzene complexes in solution.[193]

Due to this non-ideal behaviour of polyfluorobenzene-benzene systems, and because different atoms are being displaced by dissimilar mechanisms, it was considered[163] that the requirements for successful use of the competition method were not met in determining the partial rate factors [Table (4)]. Thus, the competition of hexafluorobenzene with pentafluorobenzene, bromopentafluorobenzene or octafluorotoluene for phenyl radicals were studied since these were considered to avoid the above objections.[163] The results are given in Table (5).

The fact that hydrogen is more readily displaced than fluorine in pentafluorobenzene was thought to reflect the different mechanisms by which the relevant σ-intermediates regain aromatic character.

In benzene derivatives (C_6H_5X) o-attack is preferred(o-/p- ratios greater than 2), whilst in pentafluorobenzene attack para to hydrogen is preferred (o-/p- ratios less than 2). This was explained by postulating[163] that σ-intermediates are better stabilised by o-halogens than by p-halogens as is also the case in simple benzene systems. This effect is also evident in the arylation of octafluorobenzene, and of bromopentafluorobenzene if it is considered that bromine is more effective than fluorine in the o-position.

Table (5)

Phenylation of Pentafluorobenzene, Bromopentafluorobenzene and Octafluorotoluene (80°)

C_6F_5X	$\frac{k_{C_6F_5X}}{k_{C_6F_5H}}$	Isomer Distribution (%)				Partial Rate Factors			
		X-	o-	m-	p-	Fx	Fo	Fm	Fp
C_6F_5H	0.9	29	15	45	11	1.6	0.4	1.2	0.6
C_6F_5Br	1.5	5	45	36	14	0.45	2.1	1.6	1.3
$C_6F_5CF_3$	1.2	0	5	71	24	0.0	0.2	2.7	1.8

The observation that the rate of attack of bromopentafluorobenzene relative to hexafluorobenzene (1.5) differs from that (1.0) in which both these substrates compete seperately with benzene,[7,182] was considered to arise from use of non-ideal solvent mixtures in the earlier work.

The partial rate factors [Table (5)], however, show some discrepancies and it appears that although the relative rates of attack within one molecule are readily explained, relative rates of attack between molecules are not. This discrepancy was explained by postulating the formation of complexes (similar to those known to be formed between benzene and hexafluorobenzene) between the phenyl radical, or its precursor, and the competing substrates.

In the study of the less fully fluorinated polyfluorobenzenes,[183] it was found that the partial rate factors derived from the competition of fluorobenzene and benzene ($F_{\underline{o}\text{-F}} = 1.62$, $F_{\underline{m}\text{-F}} = 1.7$, $F_{\underline{p}\text{-F}} = 0.91$) could be used to predict the relative rates of attack of polyfluorobenzenes at hydrogen-bearing sites [Table (3)]. These same partial rate factors were also used successfully to reflect the small extent of aryldefluorination occurring in the attack of the di- and trifluorobenzenes, provided an empirical factor (0.27), which was held to reflect the relative reactivities of fluorine-bearing and hydrogen-bearing sites, was incorporated. The more fully fluorinated substrates, however, showed a greater divergence between calculated and experimental figures.

The partial rate factors for aryldefluorination deduced from competition reactions between hexafluorobenzene and pentafluorobenzene ($F_{\underline{o}\text{-F}} = 2.47$, $F_{\underline{m}\text{-F}} = 0.82$, $F_{\underline{p}\text{-F}} = 1.69$) are rather different from those derived from the fluorobenzene-benzene competition reactions (see above). They give some measure of the relative rates of aryldefluorination of the tetrafluorobenzenes but then become increasingly less correct as they are applied to the less fully fluorinated systems. These partial rate factors, however, are considered to be subject to the errors caused by complex formation.[163]

I. 7. Pentafluorophenylation of Arenes

7.1 The Decomposition of Pentafluorobenzoyl Peroxide in Aromatic Solvents

From the study of partial rate factors for the phenylation of aromatic solvents (Section I. 5.), it appears that the phenyl radical is an almost neutral reagent. With substituted aryl radicals, however, the presence of a substituent might influence the distribution of electron density in the radical and impose upon it some measure of electrophilic or nucleophilic character, according to whether the substituent is electron-withdrawing or electron-repelling. This has been found to be generally the case in mono-substituted benzoyl peroxides.[6,7] The pentafluorophenyl radical should provide a very good example of a highly electrophilic aryl radical.[194]

Pentafluorobenzoyl peroxide was synthesised, independently, by Oldham,[195] by Kobrina and Yakobson,[196] and by Burdon, Campbell and Tatlow,[197] and its decomposition in aromatic solvents was investigated. A report by Oldham and Williams[198] describes the initial work.

7.1.1 Benzene

The products from the decomposition of pentafluorobenzoyl peroxide in benzene are found to be mainly pentafluorobenzoic acid and pentafluorobiphenyl, a high boiling residue and a small amount of phenyl pentafluorobenzoate.[195-198] Coleman[172] investigated the kinetics from the reaction and found it to be the same as for the benzoyl peroxide-benzene system. Thus, the mechanism is considered to be similar in type.

7.1.2 Chlorobenzene and Bromobenzene

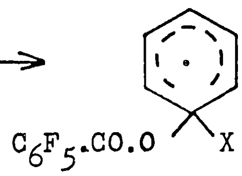
In the reaction of pentafluorobenzoyl peroxide with chlorobenzene and with bromobenzene, however, the main product is phenyl pentafluorobenzoate. Moderate yields of pentafluorobenzoic acid and residue are also formed, but only trace amounts of the chloro- and bromo- pentafluorobiphenyls are detected.[195,198] Coleman[172] found that the kinetics indicated a first-order induced decomposition of the peroxide, and also observed trace amounts of the isomeric chlorophenyl and bromophenyl pentafluorobenzoates and pentafluorobiphenyl.

Phenyl pentafluorobenzoate can only arise in these solvents by replacement of chlorine or bromine. It has been suggested[180] that owing to their electrophilicity, pentafluorobenzoyloxy radicals are stabilised by the formation of charge-transfer complexes [reaction (110)]. The formation of such complexes has already been postulated in the reaction of benzoyl peroxide and bromobenzene (Section I. 2.4[39]). This complex collapses to give a σ-intermediate [reaction (111)] via attack of C_1, the removal of the halogen atom occurring through further reaction with the aryloxy radical [reaction (112)].

$$C_6F_5CO.O\cdot \; + \; :X\text{-}Ph \longrightarrow C_6F_5CO.O^- \; \overset{+}{\cdot}X\text{-}Ph \qquad (110)$$

(XXII)

(XXII) ⟶



(111)

(XXIII)

$$(XXIII) \; + \; C_6F_5CO.O\cdot \longrightarrow C_6F_5CO.OX \; + \; C_6H_5.O.CO.C_6F_5 \qquad (112)$$

This process produces unstable hypohalite intermediates which are considered to react with hydroaromatic compounds to give both pentafluorobenzoic acid and hydrogen halide.[180]

7.1.3 Nitrobenzene

The decomposition of pentafluorobenzoyl peroxide in nitrobenzene,[198] affords mainly the isomeric nitropentafluorobiphenyls, pentafluorobenzoic acid and residue. However, trace amounts of phenyl pentafluorobenzoate and pentafluorobiphenyl are also found. The formation of such species indicates that both pentafluorobenzoyloxy and pentafluorophenyl radicals are capable of addition to the 1-position of nitrobenzene, although addition to the 2-, 3-, and 4-positions is preferred. Bolton and Williams[180] postulated that displacement of the nitro-group, by analogy, requires the formation of a complex such as (XXII) ($X = NO_2$) which either loses carbon dioxide to form (XXIV), or which itself involves the formation, not of the pentafluorobenzoate anion, but, of the pentafluorophenyl anion itself.

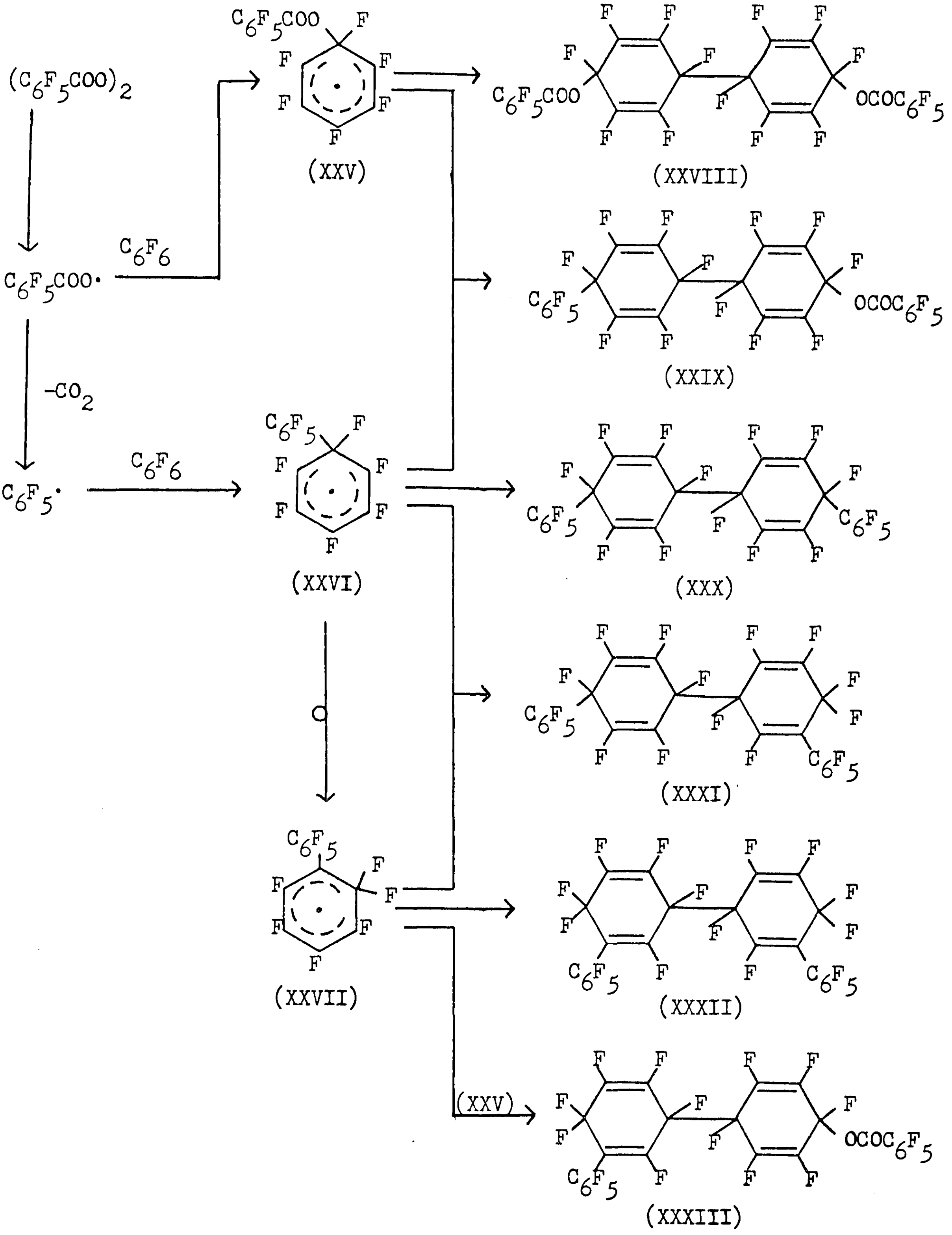
$$C_6F_5CO.O^- \overset{+}{.}NO_2\text{-Ph} \xrightarrow{-CO_2} \underset{\text{(XXIV)}}{C_6F_5^- \overset{+}{.}NO_2\text{-Ph}} \qquad (113)$$

7.1.4 Polyfluorobenzenes

The decomposition of pentafluorobenzoyl peroxide in hexafluorobenzene yields only a small amount of decafluorobiphenyl and pentafluorophenyl pentafluorobenzoate, the main product being a tarry residue.[195-198] In pentafluorobenzene a similar inertness towards biaryl formation is found, even though arylation can proceed by displacement of hydrogen as well as fluorine in this case.[197] Seabrooke[199] embarked on a study of the decomposition of pentafluorobenzoyl peroxide in a series of fluorinated benzenes. She found that in 1,2,4,5-tetrafluorobenzene arylation becomes more prominent than in hexafluorobenzene and pentafluorobenzene, hydrogen displacement to give 4-H-nonafluorobiphenyl being the major course with only a very small amount of 2,2',3,4,4',5,5',6-octafluorobiphenyl being detected. In 1,3,5-trifluorobenzene arylation by hydrogen displacement is the major course of the reaction giving 2,2',3,4,4',5,6-octafluorobiphenyl. 2,3,3',4,5,5',6-Heptafluorobiphenyl arising from fluorine displacement is not detected and only very small amounts of pentafluorobenzoic acid esters are found. In 1,4-difluorobenzene the major product besides residue is 4-fluorophenyl pentafluorobenzoate, and some 2,2',3,4,5,5',6-heptafluorobiphenyl is also formed; again, no biaryls resulting from fluorine displacement are observed. Coleman[172] had investigated the reaction of pentafluorobenzoyl peroxide in fluorobenzene and found the major products to be pentafluorobenzoic acid, phenyl pentafluorobenzoate, residue, and a small amount of 2,3,4,5,6-penatfluorobiphenyl. No isomeric hexafluorobiphenyls of fluorophenyl pentafluorobenzoates were detected.

Bolton and Williams[180] surmised that two effects were acting in opposition through the series. The first was complex formation between reagent and substrate. This was considered to be most strong with the less fully fluorinated solvents, since it is with these that the difference in polarity of the nuclei of the radicals, and of the substrate, is maximised. This complex formation brings the two reagents together, but it also stabilises the peroxide and the pentafluorobenzoyloxy radical so that arylation is only a minor process.

The second effect was ascribed to the inertness of the more fully fluorinated species towards the $C_6F_5\cdot$ radical. This was a correct deduction only in so far as the extent of reaction was deduced from the formation of the appropriate biaryls. However, in all the above mentioned reactions of pentafluorobenzoyl peroxide, the major product was a tarry residue. Kobrina[200] found that with hexafluorobenzene the main component of the residue was 4,4'-bis(pentafluorobenzoyloxy-)-1,1',4,4'-tetrahydroperfluorobiphenyl (XXVIII). Later,[201] another major component of the residue was found to be 3,3'-bis(pentafluorophenyl-)-1,1',4,4'-tetrahydroperfluorobiphenyl (XXXII). A 1,2-fluorine shift in the σ-intermediate (XXVI) formed by addition of pentafluorophenyl radical to hexafluorobenzene was proposed to account for this. The residue has now been characterised,[202] and Scheme 5 accounts for the observed products. The degree of rearrangement in σ-complex (XXVI) was found to depend on the concentration of the peroxide and on the reaction temperature.


$(C_6F_5COO)_2$
$C_6F_5COO\cdot$
C_6F_6
$-CO_2$
$C_6F_5\cdot$
C_6F_6
(XXV)
(XXVI)
(XXVII)
(XXVIII)
(XXIX)
(XXX)
(XXXI)
(XXXII)
(XXXIII)
(XXV)
C_6F_5COO
$OCOC_6F_5$
C_6F_5
F

Scheme 5.

7.2 Pentafluoroaniline with Amyl Nitrite

Since the reactions of pentafluorobenzoyl peroxide with aromatic solvents either give poor yields of biaryls or are complicated by side reactions, it had not been possible to determine partial rate factors for these reactions and thus show the electrophilicity of the pentafluorophenyl radical.

Oldham *et al.*[203] investigated the reaction of pentafluoroaniline with amyl nitrite in chlorobenzene, bromobenzene and nitrobenzene. The relative proportions of the isomeric biaryls obtained from these reactions were determined and compared with the corresponding data for phenylation of these compounds. The results (Table 6) are considered to support the postulate that pentafluorophenyl radicals display a large measure of electrophilic character.

Table (6)

Radical	Substrate	Isomer Distribution *o*-	*m*-	*p*-	Ratio (*o* + *p*)/*m*
$C_6H_5\cdot$	C_6H_5F	46.7	35.4	17.9	1.8
$C_6H_5\cdot$	C_6H_5Cl	56.9	25.6	17.5	2.9
$C_6H_5\cdot$	C_6H_5Br	55.7	28.8	15.5	2.5
$C_6H_5\cdot$	$C_6H_5NO_2$	62.5	9.8	27.7	9.2
$C_6F_5\cdot$	C_6H_5F	42	26	32	2.8
$C_6F_5\cdot$	C_6H_5Cl	64.7	20.6	14.7	3.9
$C_6F_5\cdot$	C_6H_5Br	61.6	26.3	12.1	2.8
$C_6F_5\cdot$	$C_6H_5NO_2$	20.8	53.4	25.8	0.87

Thus, with the halogenobenzenes which give the o- and p-substituted products with electrophilic reagents, the extent of o- and p-substitution is greater with pentafluorophenyl radicals than with phenyl radicals. On the other hand, this ratio is very much lower for pentafluorophenylation than phenylation of nitrobenzene wich has a strongly m-directing substituent. Sandall, Bolton and Williams[204] studied the reaction of pentafluoroaniline with amyl nitrite in fluorobenzene; they found p-substitution to be more pronounced in this solvent than in the other halogenobenzenes.

The competitive pentafluorophenylation of aromatic solvents using pentafluoroaniline with amyl nitrite has been shown to give inconsistent partial rate factors.[162] This is considered to be due to the formation of complexes between competing substrates and radicals or their precursors, as in the case of phenylation of highly fluorinated polyfluorobenzenes.[163]

7.3 Other Sources of Pentafluorophenyl Radicals

Pentafluorophenyl radicals have been reported to be formed by routes other than the decomposition of pentafluorobenzoyl peroxide and of amyl nitrite with pentafluoroaniline. These include, the oxidation of pentafluorophenyl hydrazine with silver oxide or with bleaching powder,[205] the high-temperature pyrolysis of pentafluorobenzenesulphonic acid and its chloride,[137] the photolysis and thermolysis of pentafluorohalogenobenzenes,[206-208] and, recently, the decomposition of pentafluorophenylazotriphenylmethane.[209,210] Of these, only the oxidation of pentafluorophenyl hydrazine provides high yields of biaryls when reacted with benzene.

As with the reactions of pentafluorobenzoyl peroxide and pentafluoroaniline with amyl nitrite, the oxidation of pentafluorophenyl hydrazine in hexafluorobenzene gives very little biaryl. Kobrina _et_ _al_.[209] have studied this reaction and postulated three pathways involved in the reaction. The main one consists of expulsion of hydrogen from the parent compound with formation of pentafluorobenzene. The other two processes are the attack of pentafluorophenyl radicals on hexafluorobenzene and on the parent hydrazine. The σ-complex formed by the former process appears to undergo rearrangement via a 1,2-fluorine shift prior to dimerization. This 1,2-fluorine shift has been proposed, by these same workers, for the σ-complex (XVIII) formed in the benzoyl peroxide - hexafluorobenzene system,[175] and also for the σ-complex (XXVI) formed in the pentafluorobenzoyl peroxide - hexafluorobenzene system.[201]

II. EXPERIMENTAL

II. 1. Preparation and Purification of Compounds

1.1 Benzoyl Peroxide

Moist commercial grade (B.D.H.) benzoyl peroxide was dissolved in a minimum quantity of warm chloroform and the aqueous layer rejected. The solution was rapidly filtered under suction and between two and three volumes of ice-cold methanol were added. The precipitated benzoyl peroxide was collected and further purified by repeating the above procedure at least twice. The purified benzoyl peroxide was finally filtered and dried over calcium chloride in a vacuum dessicator, m.p. 105°, (lit m.p. 104-106°).[211]

1.2 Solvents

1.2.1 Benzene

AnalaR grade benzene was allowed to stand over sodium for several days. After this time the benzene was distilled on a 2 m fractionating column packed with Fenske glass helices. The temperature of the column heating jacket and of the mantle heater for the distillation flask could be regulated by variable transformers. The temperature inside the column heating jacket was maintained at 65°. Some benzene was returned to the flask by the total reflux partial take-off still-head, and the fraction boiling at 80.5°/758 mm collected (lit. b.p. 80-80.5°/760 mm).[211]

1.2.2 Fluorinated Benzenes

The commercially available fluorinated benzenes (listed below), were distilled at atmospheric pressure, dried over magnesium sulphate and then filtered. This procedure was repeated until gas chromatographic analysis revealed the solvents to be of at least 98% purity. Solvent recovered after reaction was treated in the same manner.

	b.p.	Lit. b.p.[212]
Fluorobenzene (A)	85°	85°
1,2-Difluorobenzene (B)	92°	91°
1,3-Difluorobenzene (B)	82°	83°
1,4-Difluorobenzene (B)	88°	89°
1,2,4-Trifluorobenzene (A)	88°	88°
1,3,5-Trifluorobenzene (A)	76°	75.5°
1,2,3,4-Tetrafluorobenzene (B)	93°	95°
1,2,3,5-Tetrafluorobenzene (A)	84°	83°
1,2,4,5-Tetrafluorobenzene (A)	90°	90°
Pentafluorobenzene (B)	85°	85°
Hexafluorobenzene (A)	79°	80°

(A) - Bristol Organics Ltd.

(B) - Fluorochem Ltd.

1.3 Reference Compounds

1.3.1 4-Fluorobiphenyl

The commercially available 4-fluorobiphenyl (Aldrich Chem. Co. Ltd.) was found to be of 99% purity (gas chromatographic analysis) and it was thus used without further purification, m.p. 74°, (lit. m.p. 74.2°).[211]

1.3.2 2-Fluorobiphenyl

2-Fluorobiphenyl was prepared by the decomposition of 2-fluoroaniline with pentyl nitrite in an excess of benzene. The aniline (45 g) was dissolved in benzene (250 ml) and boiled under reflux while pentyl nitrite (30 g) was added down the condenser over 0.5 hr. The mixture was boiled until the evolution of nitrogen and oxides of nitrogen had ceased, and no further reaction resulted when a further quantity (5 ml) of the nitrite was added. The benzene was removed from the crude reaction product under reduced pressure and the biaryl was recovered by steam distillation. The crude 2-fluorobiphenyl (23 g) was recrystallised from ethanol, m.p. 74°, (lit m.p. 73.5°).[211]

1.4 Catalysts

1.4.1 Ferric Benzoate

Ferric benzoate was prepared by mixing equimolar solutions of ferric chloride and sodium benzoate. The brown precipitated ferric benzoate was boiled in water, then dried in the oven at 100° and further in a vacuum dessicator over calcium chloride.

1.4.2 Trichloroacetic Acid

The commercial grade trichloroacetic acid (May and Baker) had an assay of not less than 98%. Gas chromatographic analysis showed this to be correct and the melting point (m.p. 55-57°) was in agreement with the literature value (lit m.p. 56.3°)[211]; thus, the reagent was used without further purification.

1.5 Authentic Materials

The following, commercially available, compounds were used without further purification.

	m.p.	lit. m.p.[211]
p-Phenyl Benzoic Acid (A)	225-226°	228°
Benzoic Acid (B)	122-123°	122°
Phenyl Benzoate (B)	69°	71°
Biphenyl (B)	70-71°	71°
p-Terphenyl (B)	212°	213°

(A) - Aldrich Chem. Co. Ltd.

(B) - B.D.H.

1.6 Phenylazotriphenylmethane

Phenylhydrazotriphenylmethane was prepared by the Gomberg method[213] and oxidised to the azo-compound by a method proposed by Wieland, Popper and Seefried.[214]

Phenylhydrazine (7 ml, b.p. 137-138°)[211] in anhydrous ether (100 ml) was warmed in a flask fitted with a reflux condenser containing a calcium chloride tube. Triphenylmethyl chloride (10 g) in anhydrous ether (100 ml) was added via the condenser, followed by a further 100 ml ether. After the addition of the triphenylmethyl chloride, a white precipitate of phenylhydrazinium chloride began to form. The mixture was boiled for 3 hrs, allowed to cool, and then filtered.

To the filtrate, containing the hydrazo compound, was added 200 ml saturated bromine water, in portions, with stirring and occasional cooling. Starch iodide paper indicated the presence of excess bromine.

The aqueous layer was discarded and the ethereal solution was washed with dilute sodium bisulphite to free it from bromine, then with sodium hydroxide to remove any dissolved sulphur dioxide, and finally with water.

The ethereal layer was collected, dried over calcium chloride and filtered. Evaporation of the ether layer under reduced pressure at room temperature left a pale orange crystalline mass. This was recrystallised from chloroform-methanol to give yellow crystals of phenylazotriphenylmethane, m.p. 111-112° (lit. m.p. 113-114°)[215] with decomposition.

1.7 Polyfluoro-compounds

1.7.1 Polyfluorophenols

Some polyfluorophenols, not commercially available, were prepared by a method described by Bolton and Sandall.[216] The method involves the displacement of a fluorine atom from a polyfluorobenzene by hydroxide.

The polyfluorobenzene (3.8 g) and potassium hydroxide (4 g excess) were heated in dimethyl sulphoxide (15 ml), under reflux and with stirring, for 4 hrs. The resulting brown mixture was cooled and the inorganic material was dissolved in water (50 ml) before steam distillation removed the non-acidic organic compounds. The aqueous residue was acidified and steam distillation of this gave the polyfluorophenol which were extracted with ether, dried ($MgSO_4$) and recovered as oils when the ether was removed under reduced pressure. Table (7) lists the ^{19}F n.m.r. chemical shifts of the synthesised polyfluorophenols together with those of some commercially available materials.

Table (7)

^{19}F N.M.R. Chemical Shifts of Some Polyfluorophenols

Polyfluorophenol	Source	δ(ppm, upfield of $CFCl_3$)$^{(a)}$
2-Fluoro-	A	F_2, 141.2(138.1)^{217}
3-Fluoro-	A	F_3, 112.4(112.2)^{217}
4-Fluoro-	A	F_4, 124.6(124.0)^{217}
2,6-Difluoro-	B	F_2, 136.4(137.3)
3,5-Difluoro-	1,3,5-$F_3C_6H_3$	F_3, 109.1(108.5)
2,3,5-Trifluoro-	1,2,3,5-$F_4C_6H_2$	F_2, 169.3(168.7); F_3, 134.8(133.6); F_5, 115.4(115.2)
2,3,6-Trifluoro-	1,2,3,4-$F_4C_6H_2$	F_2, 157.5(158.7); F_3, 142.0(143.0); F_6, 140.6(140.3)
2,4,5-Trifluoro-	1,2,4,5-$F_4C_6H_2$	F_2, 142.0(143.4); F_4, 146.2(145.2); F_5, 142.0(143.0)

A - Aldrich Chem. Co. Ltd.

B - Yarsley Res. Lab.

(a) - Figures in parentheses (except when ref. 217 is quoted) refer to values derived from assuming additivity of substituent effects ($\Delta\delta_{o\text{-}F}$, 24.5; $\Delta\delta_{m\text{-}F}$, -3.9; $\Delta\delta_{p\text{-}F}$, 6.1 ppm, from difluorobenzenes) upon the figures for the monofluorophenols.

1.7.2 Polyfluorophenyl Benzoates

The polyfluorophenols [listed in table (7)] were used to prepare the corresponding polyfluorophenyl benzoates by means of the Schotten-Baumann reaction. The polyfluorophenol (1 g) was dissolved in 10% sodium hydroxide solution (15 ml) contained in a strong wide-mouthed bottle, benzoyl chloride (2 ml) was added and the mixture shaken vigorously until the benzoate precipitated (20-30 mins). The crude product was filtered, washed with water and then recrystallised from aqueous ethanol.

The mass spectrographic analysis and the melting points of the polyfluorobenzoates, thus prepared, are shown in Table (8). The infra-red analysis is shown in Table (9). Further confirmation of their identity is described later (Section II.3.5)

1.7.3 Polyfluorobiphenyls

The following polyfluorobiphenyls, prepared from the appropriate amine as in the case of 2-fluorobiphenyl (II.1.3.2), were available in the department; 2,6-difluorobiphenyl, m.p. 88°; 2,3,5,6-tetrafluorobiphenyl, m.p. 105-106° (lit m.p. 103-105°)[218] and 2,3,4,5,6-pentafluorobiphenyl, m.p. 109-110° (lit m.p. 110-112°).[205]

Table (8)

Melting Points and Mass Spectrographic Analysis of Some Polyfluorophenyl Benzoates

Polyfluorophenyl Benzoate	m.p.	Principal Features of Mass Spectrum (M/e)
2-Fluoro-	65°	217(4); 216(24); 111(5); 105(100); 83(24) (also at M/e: 77,57,51,44).
3-Fluoro-	41°	217(8); 216(45); 111(6); 105(100); 83(40) (also at M/e: 77,57,51,44,39).
4-Fluoro-	55°	217(4.5); 216(25); 111(9); 105(100); 83(35) (also at M/e: 77,57,51,44,39).
2,6-Difluoro-	64°	235(3); 234(19); 129(14); 113(3); 105(100); 101(29); 82(10); (also at M/e: 77,63,57,51,44,39).
2,3,5-Trifluoro-	33°	253(2); 252(13); 223(9); 205(4); 147(11); 141(18); 119(61); 105(100); 100(11); 81(13) (also at M/e: 77,69, 57,51,44,39).
2,3,6-Trifluoro-	39°	253(3); 252(20); 223(5); 205(3); 147(15); 141(2); 119(19); 105(100); 100(12); 81(19) (also at M/e: 77,69, 57,51,44,39).
2,4,5-Trifluoro-	41°	253(3); 252(21); 223(7); 205(5); 147(25); 141(6); 119(60); 105(100); 100(13.5); 81(20) (also at M/e: 77, 69,57,51,44,39).

Table (9)

Infrared Analysis of Some Polyfluorophenyl Benzoates

Polyfluorophenyl Benzoate	Principal Infrared Bands (cm^{-1})
2-Fluoro-	3030(w)$^{(a)}$; 1760(s)$^{(b)}$; 1600(m), 1500(s), 1460(m)$^{(c)}$; 1320-950(multiple bands)$^{(d)}$; 760(m), 710(s)$^{(e)}$.
3-Fluoro-	3030(w)$^{(a)}$; 1750(s)$^{(b)}$; 1600(m), 1490(m), 1460(m)$^{(c)}$; 1270-950(multiple bands)$^{(d)}$; 870(m), (1:3 disubst); 770(m)$^{(e)}$, 710(s)$^{(e)}$.
4-Fluoro-	3030(w)$^{(a)}$; 1760(s)$^{(b)}$; 1600(w), 1500(s), 1460(m)$^{(c)}$; 1290-1010(multiple bands)$^{(d)}$; 820(m), (1:4 disubst); 770(m), 710(s)$^{(e)}$.
2,6-Difluoro-	3030(w)$^{(a)}$; 1760(s)$^{(b)}$; 1480(m)$^{(c)}$; 1290-1020 (multiple bands)$^{(d)}$; 790(m), (1:2:3 trisubst); 770(s), 700(s)$^{(e)}$.
2,3,5-Trifluoro-	3030(w)$^{(a)}$; 1760(s)$^{(b)}$; 1630(m), 1510(s), 1450(m)$^{(c)}$; 1260-1010(multiple bands)$^{(d)}$; 880(m), (1:2:3:5 subst); 780(m), 700(s)$^{(e)}$.
2,3,6-Trifluoro-	3030(w)$^{(a)}$; 1760(s)$^{(b)}$; 1600(w), 1500(s), 1450(w)$^{(c)}$; 1320-970(multiple bands)$^{(d)}$; 800(s), (1:2:3:4 subst); 750(m), 730(s)$^{(e)}$.
2,4,5-Trifluoro-	3030(w)$^{(a)}$; 1760(s)$^{(b)}$; 1510(s), 1450(w)$^{(c)}$; 1260-1020(multiple bands)$^{(d)}$; 880(m), (1:2:4:5 subst); 770(s), 700(s)$^{(e)}$.

(a) - =C-H stretch (str.)
(b) - C=O str.
(c) - C=C in-plane str.
(d) - finger print region; C-H in-plane deformation(def.), C-F str. and C-O str.
(e) - C-H out-of-plane def. for a monosubstituted benzene.

1.7.4 Miscellaneous

The ^{19}F n.m.r. chemical shifts of the following fluoro-compounds are listed in Table (10).

(i) 1,2,3-Trifluorobenzene

2,6-Difluoroaniline (0.25 mole) was suspended in hydrochloric acid (6 M ; 125 ml) at 5-8° while sodium nitrite (17 g, 0.25 mole) in water (35 ml) was added with vigorous stirring. The solution which resulted was filtered, and treated with a saturated solution of sodium tetrafluoroborate (30 g, 0.28 mole) at below 10°. The precipitated diazonium tetrafluoroborate was carefully washed with water, ethanol, ethanol-ether, and finally ether, draining the precipitate thoroughly after each washing. The dried precipitate was carefully pyrolysed in a distillation system taking maximum precaution to avoid loss of volatile fluorocarbons. The erratic decomposition of even completely dried salt lowered the yield of 1,2,3-trifluorobenzene (purified by distillation) to 20-25%, b.p. 94° (lit. b.p. 95°).[212]

(ii) Pentafluoronitrosobenzene

Pentafluoronitrosobenzene, supplied by Bristol Organics Ltd., was used without further purification, m.p. 44-45° (lit. m.p. 44.5°).[219]

(iii) Pentafluorodiphenylamine

Pentafluorodiphenylamine was prepared by a method described by Burdon, Castaner and Tatlow.[220] A 50% w/w sodium hydride-hydrocarbon oil dispersion (2.2 g), aniline (7.7 g) and dioxan (175 ml) were refluxed for 1.5 hrs. Hexafluorobenzene (7.7 g) in dioxan (25 ml) was then added, the mixture was refluxed for a further 5 hrs, then poured into M-HCl (1.5 l) and the organic products were extracted with methylene chloride. Evaporation of the dried ($MgSO_4$) extracts left a residue, the light petroleum (b.p. 40-60°) soluble portion of which was chromatographed on alumina (30 x 3.5 cm). Elution with light petroleum-ether 4:1 v/v gave pentafluorodiphenylamine (4.3 g), m.p. 72°, (lit. m.p. 71-73°).[220]

(iv) Pentafluoroazobenzene

Pentafluoroazobenzene was made in the department by the condensation of pentafluoronitrosobenzene with aniline using a method described by J. Burdon and D.F. Thomas,[221] m.p. 91°, (lit. m.p. 92-93°).[222]

(v) Decafluorobiphenyl

Decafluorobiphenyl, supplied by Bristol Organic Ltd, was used without further purification, m.p. 69-70°, (lit. m.p. 68-69°).[165]

Table (10)

^{19}F N.M.R. Chemical Shifts of Some Fluoro-Compounds

Fluoro-Compound	δ^*(ppm, upfield of (FCl_3)
1,2,3-Trifluorobenzene[217]	F_1, 135.4(136.2); F_2, 161.8(163.0)
Pentafluoronitrosobenzene[223]	F_2, 160.1(158.1); F_3, 160.7(158.1); F_4, 142.3(141.3)
Pentafluorodiphenylamine	F_2 149.9; F_3, 163.3; F_4 163.9
Pentafluoroazobenzene[222]	F_2, 150.9(150.6); F_3, 162.8(162.2); F_4, 153.4(153.1)
Decafluorobiphenyl[217]	F_2, 137.8(140.0); F_3, 160.7(163.4); F_4, 150.4(152.0)

* - Figures in parentheses refer to literature values.

II. 2 Instrumentation

(1) N.m.r. : ^{19}F N.m.r. spectra were measured by a Joel FX 90 MHz multinuclear, Fourier-transform N.m.r. spectrometer, using a 10 mm tunable probe. Solvent, $CDCl_3$; standard, $CFCl_3$; temp, 25°c.

(2) Mass Spectroscopy : The mass spectra were measured by a V.G. Micromass 12B machine at 2-4 KV accelerating voltage and 20-70 eV ionisation potential.

(3) Gas Liquid Chromatography : G.L.C. measurements used a Pye Unicam 204 model chromatograph (FID) with a column of 15% OV1 (dimethyl silicone gum) on Chromosorb W 80/100 mesh, internal diameter 4 mm and with a nitrogen flow rate of 40 ml/min.

(4) Infrared Spectroscopy : Infrared spectra were measured on a Perkin-Elmer 197 infrared spectrometer using nujol and hexachlorobutadiene mulls on NaCl plates.

(5) G.C. - Mass Spectroscopy : The G.C.- mass spectra were measured using the University College (London) Chemistry department facilities, a V.G. Micromass 70-70 m.s. instrument coupled with a Pye 104 gas chromatograph were made available by the kind permission of Prof. J.H. Ridd.

II. 3. The Decomposition of Benzoyl Peroxide in Polyfluorobenzenes

3.1 General Method of Reaction

Benzoyl peroxide was allowed to react with a number of polyfluorobenzenes using the following experimental method. Accurately weighed amounts of benzoyl peroxide (*ca* 10^{-3} mole), the reference compound (*ca* 0.1 g) and the catalyst (where appropriate) were mixed with the purified solvent (5.0 ml) in a 20 ml flask and shaken to allow solution. One or two small lumps of carbon dioxide were added to displace atmospheric oxygen. The thermolysis was carried out in an oil thermostat at 80 $\pm 1^{\circ}$C over 72-100 hours after which no further decomposition took place.

3.2 Isolation of Products by Steam Distillation

At the end of the reaction period, the excess of polyfluorobenzene solvent was removed from the crude reaction products by careful distillation (water bath). The recovered solvent was checked (G.L.C. analysis) for biaryl impurities. The resulting residue was exhaustively steam distilled. The steam-volatile materials were extracted with chloroform. The extracts were dried ($MgSO_4$), filtered and then evaporated to dryness.

3.3 Identification and Estimation of the Steam-Volatile Polyfluorobiphenyl Products

The steam volatile polyfluorobiphenyls resulting from the reaction of benzoyl peroxide with polyfluorobenzenes were analysed using ^{19}F n.m.r; G.L.C. was also used but only as a confirmatory technique.

3.3.1 Identification

The polyfluorobiphenyls were identified by ^{19}F n.m.r. analysis on the basis: (a) that the number and relative intensities of the absorptions were consistent with assignment, (b) that the chemical shifts agreed with those already obtained,[183] (c) that where the same compound was found in two different systems, the detailed ^{19}F n.m.r. spectra agreed in both cases and (d) that, in some cases, the ^{19}F n.m.r. spectra agreed with those found for authentic samples.

The ^{19}F n.m.r. chemical shifts used in analysis of the polyfluorobiphenyls are listed in Table (11). They are all measured relative to trichlorofluoromethane ($CFCl_3$ = 0.00 ppm) with deuterated chloroform as solvent. The absorption peak of a fluorine atom can be up to 1.0 ppm wide, thus, the chemical shifts that are quoted refer to the centre point of the peak. It is not possible to reproduce readings to better than 0.1 ppm. There are several factors that may contribute to this error. The information from the Jeol FX 90 MHz n.m.r. spectrometer is stored in 8192 channels and thus a sweep width of 5000 Hz (the normal width used) leads to a resolution of 0.61 Hz per channel which corresponds to 0.007 ppm. However, larger errors are observed due to factors such as (1) variation in the purity of samples, (2) solvent effects, (3) interactions between molecules and (4) variations in the concentration of the solutions.

3.3.2 Estimation

The fluorinated biphenyl yields were estimated by intergrating the ^{19}F n.m.r. absorption peaks. The integral of the peak from the internal standard (4-fluorobiphenyl or 2-fluorobiphenyl) was taken as

Table (11)

^{19}F N.M.R. Shifts used in Analysis of Fluorinated Biphenyls$^{(a)}$

Substituents	δ(ppm, upfield of $CFCl_3$)
2-Fluoro-	118.6
3-Fluoro-	113.7
4-Fluoro-	116.4
2,3-Difluoro-	F_2, 144.3(143.1); F_3, 138.4(138.2)
2,4-Difluoro-	F_2, 114.2(114.3); F_4 112.2(112.5)
2,5-Difluoro-	F_2, 124.7(124.7); F_5, 119.6(119.8)
2,6-Difluoro-	F_2, 115.1(114.7)*
3,4-Difluoro-	F_3, 138.0(138.2); F_4, 140.8(140.9)
3,5-Difluoro-	F_3, 110.3(109.8)
2,3,4-Trifluoro-	F_2, 139.4(139.2); F_3, 160.5(162.7); F_4, 136.6(136.7)
2,3,5-Trifluoro-	F_2, 149.1(149.2); F_3, 133.3(134.5); F_5, 116.0(115.9)
2,3,6-Trifluoro-	F_2, 138.5(139.2); F_3, 142.6(143.9); F_6, 120.4(120.8)
2,4,5-Trifluoro-	F_2, 120.0(120.3); F_4, 135.7(136.7); F_5, 143.4(143.9)
2,4,6-Trifluoro-	F_2, 111.9(111.2); F_4, 109.5(108.6)
3,4,5-Trifluoro-	F_2, 134.6(134.3); F_4, 166.2(165.4)
2,3,4,5-Tetrafluoro-	F_2, 144.3(144.5); F_3, 155.7(156.6); F_4, 157.7(160.2)
	F_5, 140.2(140.4)
2,3,4,6-Tetrafluoro-	F_2, 136.0(135.5); F_3, 165.3(166.6); F_4, 133.9(134.0)
	F_6, 118.6(116.9)
2,3,5,6-Tetrafluoro-	F_2, 144.6(144.6)*; F_3, 139.7(139.4)*
2,3,4,5,6-Pentafluoro-	F_2, 143.8(143.8)*; F_3, 162.9(162.8)*; F_4, 156.3(156.2)*

(a) Figures in parentheses refer either to values found for samples of authentic material, or to values derived from assuming additivity of substituent effects ($\Delta\delta_{o-F}$, 24.5; $\Delta\delta_{m-F}$, -3.9; $\Delta\delta_{p-F}$, 6.1 ppm, from the difluorobenzenes) upon the figures for the monofluorobiphenyls.
Those marked with an asterisk refer to values for authentic materials.

the reference to which the integrals of all the other peaks were compared using the technique of 'spotting' (see Jeol, FX 90Q F.T. n.m.r. spectrometer handbook). Using a control experiment this technique was found to be accurate to 1 %. The largest contribution to the error was noise, this could be minimised by increasing the number of pulses given to the sample.

For each non-equivalent fluorine atom in a compound there is an absorption peak which has the same integration value relative to the standard. This was not always found experimentally. Factors contributing to the difference are (1) overlap with peaks of other compounds, (2) noise (as mentioned above) and (3) incomplete resolution of peaks. The product yields are, on this account, expected to be accurate to within 3 % of each value.

3.4 Polyfluorobiphenyl Product Yields

Benzoyl peroxide was allowed to decompose in a number of fluorinated benzenes (1) in the absence of additive, (2) in the presence of ferric benzoate and (3) in the presence of trichloroacetic acid. The reactions were carried out using the method described in Section (II. 3.1), and the resulting polyfluorobiphenyls were isolated by steam distillation (II. 3.2) and then identified and estimated using ^{19}F n.m.r. (II. 3.3). The observed polyfluorobiphenyl yields and isomer distributions from the thermolysis of benzoyl peroxide in polyfluorobenzenes in the absence of additive are listed in Table (12). The yields are quoted as (moles of biaryl per mole of peroxide decomposed) x 100. Reactions which were duplicated, and those which could be compared with previously published results [see (I. 6.3), Table (3)] each showed agreement to within 3 % in the isomer distributions although larger differences between the observed yields were sometimes found.

The results obtained for the decomposition of benzoyl peroxide in polyfluorobenzenes in the presence of ferric benzoate are tabulated in Table (13) and those obtained in the presence of trichloroacetic acid are listed in Table (14).

Table (12)

See key penultimate page.

Yields of Polyfluorobiphenyls from the Decomposition of Benzoyl Peroxide in Polyfluorobenzenes (80°; 72-100 h) in the Absence of Additives

Polyfluorobenzene	Biaryl	Yield*	Isomer (exp)	Ratio (calc)**
B	2	5.8	9	15
	3	30.1	50	27
	4	13.3	21	13
	1	12.8	20	45
C	5	7.4	18	15
	6	19.8	49	28
	2	13.6	33	57
D	7	4.7	9	11
	8	15.8	29	10
	9	1.6	3	4
	3	32.4	59	75
E	10	16.5	26	23
	4	47.1	74	77
F	11	4.1	8	8
	8	50.8	92	92

(continued)

Table (12) (cont.)

Polyfluorobenzene	Biaryl	Yield*	Isomer (exp)	Ratio (calc)**
G	12	3.3	6	6
	13	3.6	7	6
	14	<1.0	<1	3
	7	15.9	30	23
	6	19.5	37	40
	10	10.1	19	22
H	15	7.4	11	14
	16	39.1	59	56
	14	19.8	30	30
I	17	-	-	5
	12	21.8	39	39
	18	21.7	39	35
	11	12.2	22	21
J	19	<1.0	<2	6
	13	70.4	>98	94

* (Mole of biaryl / mole of peroxide decomposed) x 100

** Using partial rate factors (f_{o-F}, 2.0; f_{m-F}, 1.1; f_{p-F}, 1.1) derived from competitive phenylation reactions of fluorobenzene with benzene.[161]

Table (13)

See key penultimate page

Yields of Polyfluorobiphenyls from the Decomposition of Benzoyl Peroxide in Polyfluorobenzenes 80 ± 1°; 72-100 h) in the Presence of Ferric Benzoate

Polyfluorobenzene	Amount of Additive (g)	Biaryl	Yield*	Isomer Ratio
B	0.13	2	6.1	11
		3	24.5	45
		4	7.6	14
		1	16.6	30
C	0.10	5	8.1	15
		6	18.9	36
		2	15.6	49
D	0.10	7	2.7	7
		8	10.8	28
		9	1.2	3
		3	23.7	62
E	0.10	10	11.9	22
		4	43.3	78
F	0.09	11	3.8	5
		8	75.8	95

(continued)

Table (13) (cont.)

Polyfluorobenzene	Amount of Additive (g)	Biaryl	Yield*	Isomer Ratio
G	0.08	12	2.9	5
		13	2.9	5
		14	2.2	4
		7	16.5	27
		8	22.9	38
		10	12.9	21
H	0.09	15	7.0	9
		16	41.9	57
		14	25.2	34
I	0.07	17	-	-
		12	22.4	41
		18	23.1	42
		11	9.8	17
J	0.08	19	<1	<2
		13	65.6	>98

* (Moles of biaryl per mole of peroxide decomposed) x 100

Table (14)

See key penultimate page.

Yields of Polyfluorobiphenyls from the Decomposition of Benzoyl Peroxide in Polyfluorobenzenes (80° ±1; 72-100 h) in the Presence of Trichloroacetic Acid

Polyfluorobenzene	Amount of Additive (g)	Biaryl	Yield*	Isomer Ratio
B	0.16	2	6.0	10
		3	31.2	53
		4	10.2	18
		1	10.8	19
C	0.17	5	5.0	14
		6	17.7	48
		2	13.9	38
D	0.15	7	5.8	11
		8	15.6	30
		9	1.6	3
		3	29.7	56
E	0.15	10	20.2	35
		4	37.5	65
F	0.14	11	3.9	7
		8	52.7	93

(continued)

Table (14) (cont.)

Polyfluorobenzene	Amount of Additive (g)	Biaryl	Yield*	Isomer Ratio
G	0.16	12	3.5	7
		13	4.5	9
		14	1.8	4
		7	12.5	26
		6	15.9	33
		10	10.4	21
H	0.15	15	6.3	13
		16	28.1	56
		14	15.5	31
I	0.18	17	-	-
		12	20.5	41
		18	19.2	39
		11	9.8	20
J	0.15	19	<1	<2
		13	40.2	>98

* (Moles of biaryl per mole of peroxide decomposed) x 100.

3.5 Identification and Estimation of the Steam-Volatile Polyfluorophenyl Benzoate Products

3.5.1 Identification

The polyfluorophenyl benzoates observed as steam-volatile products from the decomposition of benzoyl peroxide in polyfluorobenzenes were identified by the following methods.

(1) Gas chromatographic analysis (using an OVI column, temp. 150°c) showed that the retention times of these esters are much longer than those of the biaryls and of the same order as that of phenyl benzoate.

(2) When the reaction mixtures were shaken with sodium hydroxide and then re-analysed by G.L.C. the peaks assigned to the fluorinated phenyl benzoates had disappeared.

(3) The ^{19}F n.m.r. coupling constants and chemical shifts agreed with those predicted.

(4) In some cases, the polyfluorophenyl benzoate was identified by agreement of the ^{19}F n.m.r. spectrum and G.L.C. retention time with that of an authentic sample prepared from the corresponding phenol as described in Section (II. 1.3.3). Table (15) lists the ^{19}F n.m.r. chemical shifts used in the analysis of the fluorinated phenyl benzoates. As with those for the polyfluorobiphenyls (II. 3.3.1), the ^{19}F n.m.r. chemical shifts for polyfluorophenyl benzoates are measured relative to trichlorofluoromethane ($CFCl_3$ = 0.0 ppm), using $CDCl_3$ as solvent, and are quoted to one decimal place with a probable error of ± 0.1 ppm.

Table (15)

^{19}F N.M.R. Shifts used in Analysis of Fluorinated Phenyl Benzoates

Substituent	δ(ppm, upfield of $CFCl_3$)$^{(a)}$
2-Fluoro-	128.9$^{(b)}$
3-Fluoro-	111.5$^{(b)}$
4-Fluoro-	117.6$^{(b)}$
2,3-Difluoro-	F_2, (153.4); F_3, (136.0)
2,4-Difluoro-	F_2, 124.2(125.0); F_4 113.3(113.7)
2,5-Difluoro-	F_2, 134.3(135.0); F_5, 117.3(117.6)
2,6-Difluoro-	F_2, 126.5$^{(c)}$(125.0)
3,4-Difluoro-	F_3, 135.8(136.0); F_4, 141.7(142.1)
3,5-Difluoro-	F_3, 113.1
2,3,4-Trifluoro-	F_2, 146.4(149.5); F_3, 158.0(160.5); F_4, 137.0(138.2)
2,3,5-Trifluoro-	F_2, 156.3$^{(c)}$(159.5); F_3, 132.9$^{(c)}$(132.1); F_5, 115.0$^{(c)}$(113.7)
2,3,6-Trifluoro-	F_2, 147.5$^{(c)}$(149.5); F_3, 140.8(142.1); F_6, 131.0$^{(c)}$(131.1)
2,4,5-Trifluoro-	F_2, 129.7, 129.7$^{(c)}$(131.1); F_4, 136.8, 136.7(138.2) F_5, 140.8, 140.6$^{(c)}$(142.1)
2,4,6-Trifluoro-	F_2, 122.8(121.1); F_4, 110.3(109.8)
3,4,5-Trifluoro-	F_3, (132.1); F_4, (166.6)

(a) - The figures in parentheses refer to values derived from assuming additivity of substituent effects ($\Delta\delta_{o-F}$, 24.5; $\Delta\delta_{m-F}$, -3.9; $\Delta\delta_{p-F}$, 6.1 ppm, from the difluorobenzenes) upon the figures for the monofluorophenyl benzoates.

(b) - The figures for the monofluorophenyl benzoates refer to the values found for the authentic materials as well as those found from the reaction mixtures.

(c) - These figures refer to values found for samples of the authentic polyfluorophenyl benzoate materials.

3.5.2 Estimation

The polyfluorophenyl benzoate yields were estimated by integrating the ^{19}F n.m.r. absorbtion peaks using the method described in Section (3.3.2) and each value is subject to no more than 3% error. The observed polyfluorophenyl benzoate yields from the decomposition of benzoyl peroxide (1) in the absence of additive (2) in the presence of ferric benzoate and (3) in the presence of trichloroacetic acid, are tabulated in Table (16).

Table (16)

Yields of Polyfluorophenyl Benzoates from the Decomposition of Benzoyl Peroxide in some Polyfluorobenzenes in the Presence and Absence of Additives (80 ± 1°c; 72-100 h)

Polyfluorobenzene	Polyfluorophenyl Benzoate	Yield* (a)	Yield* (b)	Yield* (c)
1,2,3,4-Tetrafluoro-	2,3,4-Trifluoro-	4.3	-	7.4
	2,3,6-Trifluoro-	-	-	-
1,2,3,5-Tetrafluoro-	2,3,5-Trifluoro-	-	-	-
	2,4,6-Trifluoro-	<1	-	5.6
	3,4,5-Trifluoro-	<1	-	2.8
1,2,4,5-Tetrafluoro-	2,4,5-Trifluoro-	7.0	5.1	21.0
1,3,5-Trifluoro-	3,5-Difluoro-	-	-	2.9
1,2,4-Trifluoro-	2,4-Difluoro-	5.8	2.2	16.6
	2,5-Difluoro-	<1	-	4.2
	3,4-Difluoro-	1.8	<1	9.0
1,2-Difluoro-	2-Fluoro-	2.3	2.2	12.2
1,3-Difluoro-	3-Fluoro-	-	-	4.2
1,4-Difluoro-	4-Fluoro-	6.0	1.4	34.0

(*) - (Moles of ester per mole of peroxide decomposed) x 100.

(a) - In the absence of additives.

(b) - In the presence of ferric benzoate.

(c) - In the presence of trichloroacetic acid.

3.6 Further Thermolysis of Residues obtained from the Decomposition of Benzoyl Peroxide in 1,3,5-Trifluorobenzene and 1,2,3,4-Tetrafluorobenzene

The non-steam volatile residues from the decomposition of benzoyl peroxide in 1,3,5-trifluorobenzene or 1,2,3,4-tetrafluorobenzene were dissolved in benzene (5 ml), placed in an oil bath maintained at 80 ± 1°c, and allowed to react over a prolonged period of time (ca 14 days). At the end of this time the excess of benzene was removed by distillation and the resulting residue exhaustively steam distilled. The steam volatile products, that were thus obtained, were analysed. Those from 1,3,5-trifluorobenzene were analysed by G.C.- mass spectroscopy [Table (17)] and those from 1,2,3,4-tetrafluorobenzene by mass spectroscopy [Table (18)].

Table (17)

Some Products of Further Thermolysis (14 days; 80° ± 1 c) of the Non-Steam Volatile Residue from the Decomposition of Benzoyl Peroxide in 1,3,5-trifluorobenzene

No.[(a)]	Proposed Assignment	Principal Features of Mass Spectrum (M/e)
1	Benzoic Acid	123(6); 122(82); 105(100); 77(73), 51(35)
2	Biphenyl carboxylic acid	198(2); 105(100); 77(41); 51(2)
3	2,4,6-Trifluoro-o-terphenyl	284(4); 265(2); 206(100); (Also peaks at M/e: 177,157,151,103,77,51)
4	2',5'-Difluoro-p-terphenyl	267(9); 266(100); 251(18); 245(8); 122(8); 119(3)
5	4'-Fluoro-m-terphenyl	249(18); 248(100); 233(27); 227(19); 220(17); 123(14); 113(6); (Also peaks at M/e: 215,207,194,183,170,157,144, 133,110,105,101,97,87,77,51)
6	2,3,4,6-Tetrafluoro-m-terphenyl	302(4.6); 284(5.6); 223(3); 205(2.6); 149(100); 105(2.6); (Also peaks at M/e: 93,76,65,57,41)
7	2',4',6'-Trifluoro-m-terphenyl	285(19); 284(100); (Also peaks at M/e: 262,256,236,206,151,142,131,119,106, 77,63,51,39)
8	2,6-Difluoro-p-benzoyloxybiphenyl	310(2); 266(19); 105(100); 77(27); (Also peaks at M/e: 205,181,151,133,51)

(continued)

Table (17) (cont.)

No.[a]	Proposed Assignment	Principal Features of Mass Spectrum (M/e)
9	4-Fluoroterphenyl	249(17); 248(100); (Also peaks at M/e: 233,266,220,207,194,183,170, 124,110,105,97,85,77,63,51,40)
10	$C_6H_5.C_6H_2F_2.C_6H_2F_2C_6H_5$	379(24); 378(100); 301(26); 281(12); (Also peaks at M/e: 363,358,337,230, 189,168,158,139,113,101,77,51)
11	4,6-Difluoro-o-benzoyloxy-biphenyl	311(2); 310(6); 206(2); 177(2); 157(2); 151(2); 105(100); 77(27); 51(2)
12	$C_6H_5.C_6F_2H_2.C_6F_2H_2.C_6H_5$	379(24); 378(100); 363(14); 358(12); (Also peaks at M/e: 343,336,325,313, 300,280,189,168,77,51)

(a) Elution order on G.C.- Mass Spectrum.

Table (18)

Some Products of Further Thermolysis (14 days; 80 ± 1°c) of the Non-Steam Volatile Residue from the Decomposition of Benzoyl Peroxide in 1,2,3,4-Tetrafluorobenzene

Assignment	Principal Features of Mass Spectrum (M/e)
(Ph.CO.O.$C_6H_3F_4$)$_2$- HF	522(8; M/M=1, 1/.29); 502(5)$^{(a)}$; 484(4); 468(3); 428(7); 414(17; M/M+1, 1/.3)$^{(b)}$; 394(5); 354(8); 324(9); 314(7); 302(4)$^{(c)}$; 284(30; M/M+1, 1/.26)$^{(c)}$; 224(58); 205(18); 181(42); 198(6)$^{(c)}$; 149(25); 122(57)$^{(c)}$; 105(100); (Also peaks at M/e: 91,85,77,71,57,51).

(a) Isomeric Ph.CO.O.C_6F_3H.C_6F_3H.O.CO.Ph

(b) Isomeric Ph.C_6F_3H.C_6F_3H.Ph

(c) Isomers (anticipated in this specific system) of compounds proposed for the 1,3,5-trifluorobenzene, see Table (17).

II. 4 The Competitive Phenylation Reactions of Benzoyl Peroxide in Mixtures of Polyfluorobenzenes

4.1 General Reaction Method

Benzoyl peroxide (0.25 g) was decomposed in a number of polyfluorobenzene mixtures (5.0 ml). For each combination of polyfluorobenzenes, two experiments were carried out. In one, the proportions of one of the fluorinated benzenes to the other was 3:2 v/v and in the other experiment the proportions were 2:3 v/v. One or two small lumps of carbon dioxide were added to the reaction mixtures before they were allowed to react over 72-100 hrs at 80 ± 1°c. At the end of this period a known amount of the internal standard (4-fluorobiphenyl or 2-fluorobiphenyl) was added. The fluorinated biphenyls were then isolated as outlined in Section (II. 3.2), identified and estimated (II. 3.3).

4.2 Yields of Fluorinated Biphenyls

Using the method outlined in the above section yields of polyfluorobiphenyls [(mole of biaryl per mole of benzoyl peroxide decomposed) x 100] were determined for the decomposition of benzoyl peroxide in a number of polyfluorobenzene mixtures. The results are tabulated in Tables (19)-(22). The observed yields are expected to be within 3% of each value.

Table (19)

See key penultimate page.

Biaryl Yields from the Decomposition of Benzoyl Peroxide in a Mixture of Hexafluorobenzene (A) and Polyfluorobenzene ($C_6F_XH_{6-X}$)

Polyfluorobenzene Mixture	Biaryls	Yield* (a)	%** (a)	Yield* (b)	%** (b)
A/C	1	41.8	70	30.3	49
	5	1.6	3	2.8	5
	6	5.9	10	12.0	20
	2	9.9	17	16.1	26
A/D	1	50.2	72	34.8	55
	7	1.2	2	1.8	3
	8	3.6	5	6.1	10
	9	-	-	<1	<1
	3	14.7	21	19.0	31
A/E	1	35.2	56	22.7	32
	10	3.9	6	6.2	9
	4	24.0	38	41.1	59
A/F	1	32.2	73	33.1	61
	11	0.85	2	2.4	4
	8	10.9	25	19.1	35

(continued)

Table (19) (cont.)

Polyfluorobenzene Mixture	Biaryls	Yield*	%**	Yield*	%**
		(a)		(b)	
$\frac{A}{G}$	1	31.1	58	20.2	42
	12	<1	<1	1.8	4
	13	<1	<1	1.1	2
	14	<1	<1	0.9	2
	7	7.2	13	7.9	17
	6	8.1	15	10.7	22
	10	4.2	8	5.2	11
$\frac{A}{H}$	1	57.0	58	31.6	39
	15	2.6	3	4.2	6
	16	27.9	28	31.0	39
	14	10.6	11	13.2	16
$\frac{A}{I}$	1	56.8	72	38.6	52
	17	-	-	-	-
	12	7.7	10	12.8	17
	18	11.1	14	17.4	23
	11	3.2	4	5.7	8
$\frac{A}{J}$	1	29.2	38	17.3	22
	19	<1	<1	<1	<1
	13	46.4	61	60.5	78

(a) - 3 ml C_6F_6 : 2 ml $C_6F_XH_{6-X}$

(b) - 2 ml C_6F_6 : 3 ml $C_6F_XH_{6-X}$

(*) - (Moles of biaryl per mole of peroxide decomposed) x 100

(**)- Percentage of the total yield of biaryls

Table (20)

See key penultimate page.

Biaryl Yields From the Decomposition of Benzoyl Peroxide in a Mixture of 1,2-Difluorobenzene (H) and Polyfluorobenzene ($C_6F_XH_{6-X}$)

Polyfluorobenzene Mixture	Biaryls	(a)		(b)	
		Yield*	%**	Yield*	%**
$\frac{H}{C}$	15	5.0	8	4.7	7
	16	22.4	35	15.3	22
	14	15.7	24	13.6	20
	5	3.8	6	5.1	8
	6	8.3	13	14.8	21
	2	8.9	14	15.3	22
$\frac{H}{D}$	15	4.5	8	3.5	6
	16	22.8	39	19.2	31
	14	15.8	27	13.4	22
	7	1.9	3	3.5	6
	8	3.9	7	6.7	11
	9	<1	<1	1.4	2
	3	9.0	15	13.4	22
$\frac{H}{E}$	15	5.7	8	3.4	5
	16	22.2	31	15.7	23
	14	16.9	24	13.4	19
	10	7.2	10	10.0	14
	4	19.4	27	27.2	39

(continued)

Table (20) (cont.)

Polyfluorobenzene Mixture	Biaryls	(a) Yield*	(a) %**	(b) Yield*	(b) %**
$\frac{H}{F}$	15	5.1	9	4.0	8
	16	25.6	45	18.8	36
	14	15.6	27	11.9	23
	11	0.9	2	1.3	2
	8	9.8	17	16.1	31
$\frac{H}{I}$	15	2.9	5	1.8	4
	16	23.4	40	14.9	29
	14	13.4	23	7.9	16
	17	-	-	-	-
	12	7.4	13	10.3	20
	18	8.4	14	11.6	23
	11	2.7	5	4.2	8
$\frac{H}{J}$	15	4.4	6	4.0	5
	16	20.3	28	15.4	19
	14	12.1	17	9.9	12
	19	<1	<1	<1	<1
	13	35.0	48	49.8	63

(a) - 3 ml 1,2-$C_6F_2H_4$: 2 ml $C_6F_XH_{6-X}$

(b) - 2 ml 1,2-$C_6F_2H_4$: 3 ml $C_6F_XH_{6-X}$

(*) - (Moles of biaryl per mole of peroxide decomposed) x 100

(**)- Percentage of the total yield of biaryls

Table (21)

See key penultimate page.

Biaryl Yields From the Decomposition of Benzoyl Peroxide in a Mixture of 1,4-Difluorobenzene (J) and Polyfluorobenzene ($C_6F_XH_{6-X}$)

$J/C_6F_XH_{6-X}$	Biaryls	(a) Yield*	(a) %**	(b) Yield*	(b) %**
$\frac{J}{C}$	19	<1.0	<1	<1.0	<1
	13	49.1	75	35.9	57
	5	2.7	4	4.5	7
	6	7.7	12	12.9	2
	2	5.5	8	9.3	1
$\frac{J}{D}$	19	<1.0	<1	<1.0	<1
	13	52.8	76	42.7	62
	7	2.3	3	4.2	6
	8	4.0	6	6.5	10
	9	1.0	2	1.7	3
	3	8.0	12	12.8	18
$\frac{J}{E}$	19	<1.0	<1	<1.0	<1
	13	59.3	72	32.2	46
	10	6.4	8	9.9	14
	4	15.6	19	26.8	39

(continued)

Table (21) (cont.)

$J/C_6F_XH_{6-X}$	Biaryls	(a)		(b)	
		Yield*	%**	Yield*	%**
$\frac{J}{F}$	19	<1.0	<2	<1.0	<1
	13	55.3	84	44.5	74
	11	<1.0	<2	<1.0	<1
	8	7.7	12	14.2	24
$\frac{J}{I}$	19	<1.0	<1	<1.0	<2
	13	47.9	75	36.5	57
	17	-	-	-	-
	12	6.4	10	10.5	16
	18	5.9	9	11.5	18
	11	3.0	5	4.9	8

(a) - 3 ml 1,4-$C_6F_2H_4$: 2 ml $C_6F_XH_{6-X}$

(b) - 2 ml 1,4-$C_6F_2H_4$: 3 ml $C_6F_XH_{6-X}$

(*) - (Moles of biaryl per mole of peroxide decomposed) x 100

(**)- Percentage of the total yield of biaryl

Table (22)

See key penultimate page.

Biaryl Yields From the Decomposition of Benzoyl Peroxide in a Mixture of 1,2,3,4-Tetrafluorobenzene (C) or 1,2,4,5-Tetrafluorobenzene (E) and another Polyfluorobenzene $(C_6F_XH_{6-X})$

Polyfluorobenzene Mixture	Biaryl	(a)		(b)	
		Yield*	%**	Yield*	%**
$\frac{C}{F}$	5	6.5	12	2.9	6
	6	15.9	30	9.7	22
	2	16.3	31	9.8	22
	11	1.4	3	1.6	4
	8	13.0	24	20.8	46
$\frac{C}{I}$	5	3.3	8	2.3	5
	6	11.2	27	6.9	15
	2	8.2	20	4.9	11
	17	-	-	-	-
	12	7.0	17	12.4	27
	18	8.4	20	13.6	30
	11	3.3	8	5.6	12
$\frac{E}{D}$	10	10.3	17	6.9	14
	4	34.1	58	22.2	43
	7	1.3	2	1.7	3
	8	3.2	5	5.4	11
	9	<1.0	<1	<1.0	<2
	3	9.0	15	14.1	27

(continued)

Table (22) (cont.)

Polyfluorobenzene Mixture	Biaryl	(a) Yield*	(a) %**	(b) Yield*	(b) %**
E/F	10	8.9	18	5.7	13
	4	30.7	63	20.8	48
	11	0.6	1	2.8	6
	8	8.5	18	14.2	33
E/I	10	10.8	16	7.4	12
	4	28.7	43	20.9	35
	17	-	-	-	-
	12	10.9	17	13.0	21
	18	10.2	15	13.7	23
	11	5.6	9	5.5	9

(a) - 3 ml $C_6F_4H_2$ (C) or (E) : 2 ml $C_6F_XH_{6-X}$

(b) - 2 ml $C_6F_4H_2$ (C) or (E) : 3 ml $C_6F_XH_{6-X}$

(*) - (Mole of biaryl per mole of peroxide decomposed) x 100

(**)- Percentage of the total yield of biaryl

4.3 The Measurement of Partial Rate Factors

The measurement of partial rate factors compares two competing sites. When benzoyl peroxide is allowed to decompose in an equimolar solution of polyfluorobenzenes A and B, the partial rate factor (f_i) is defined as:

$$\frac{\text{rate of attack at one specified site in A}}{\text{rate of attack at one specified site in B}} = f_i \tag{114}$$

The rate of attack is considered to be the ratio of the molar yield of the biaryl produced by attack at that site and the number of equivalent sites, thus:

$$f_i = \frac{M_{A'}/n_A}{M_{B'}/n_B} \tag{115}$$

where $M_{A'}$ = molar yield of product A' from attack at a specific site in A.

$M_{B'}$ = molar yield of product B' from attack at a specific site in B.

n_A and n_B = number of equivalent sites in A and in B respectively.

In a non-equimolar mixture of $\underline{x}$ g of A (M.W. = X) and $\underline{y}$ g of B (M.W. = Y), the number of moles of each is $\underline{x}$/X and $\underline{y}$/Y respectively. Using V_A ml of A and V_B ml of B, the number of moles of A and B are:

$(V_A d_A/X)$ and $(V_B d_B/Y)$ respectively.

where V = volume (ml)

d = density

X and Y = Molecular weight of A and B respectively.

Thus one mole of A is mixed with $(V_A.d_A/Y)/(V_A.d_A/X)$ moles of B.

$= (V_B.d_B.X)/(V_A.d_A.Y)$ moles of B = H

For equimolar amounts of A and B, the observed amount of B' is reduced by the factor H.

Thus the molar ratio of A'/B' is $M_{A'}/(M_{B'}/H) = (M_{A'}H)/M_{B'}$

$$\text{and } f_i = M_{A'}.n_B.H/M_{B'}.n_A = M_{A'}.n_B.V_B.d_B.X/M_{B'}.n_A.V_A.d_A.Y \qquad (117)$$

In mixtures of polyfluorobenzenes A and B, f_i is a ratio of the product(s) of the appropriate fluorine substituent rate factors f_o, f_m, f_p, where o, m and p refer to the relative orientation(s) of substituent(s) and the reaction site.

The partial rate factors (f_i) for competitive phenyldefluorination reactions are listed in Tables (23)-(25), those for competitive phenyldehydrogenation reactions are tabulated in Tables (26)-(28). The density measurements used are those quoted in 'Rodd's Chemistry of Carbon Compounds'.[212]

Table (23)

See key penultimate page.

Partial Rate Factors for Competitive Phenyl Defluorination Reactions in Mixtures of Hexafluorobenzene (A) and Polyfluorobenzene ($C_6F_XH_{6-X}$)

$C_6F_XH_{6-X}$	Site of Attack on $C_6F_XH_{6-X}$	f_i ratio*	(a) $M_{A'}/M_{B'}$**	(a) f_i	(b) $M_{A'}/M_{B'}$**	(b) f_i
C	C-1	$f_o f_m$	41.8/1.6	6.33	30.3/2.8	6.11
	C-2	$f_m f_p$	41.8/5.9	1.72	30.3/12.0	1.38
D	C-1	$f_o f_p$	50.2/1.2	10.0	34.8/1.8	10.4
	C-2	$f_m{}^2$	50.2/3.6	1.67	34.8/6.5	1.54
E	C-1	$f_o f_m$	35.2/3.9	4.4	22.7/6.2	4.27
F	C-1	$f_o^2 f_p$	32.2/0.9	14.0	33.1/2.4	11.5
H	C-1	$f_o f_m^2 f_p$	57.0/2.6	5.65	31.6/4.2	4.36

(a), (b), (*), (**) See page 117 for details.

Table (24)

See key penultimate page.

Partial Rate Factors for Competitive Phenyl Defluorination Reactions in Mixtures of 1,2-Difluorobenzene [(H); (C-1)] and Polyfluorobenzene ($C_6F_XH_{6-X}$)

				(a)		(b)
$C_6F_XH_{6-X}$	Site of Attack on $C_6F_XH_{6-X}$	f_i ratio*	$M_{A'}/M_{B'}$**	f_i	$M_{A'}/M_{B'}$**	f_i
C	C-1	$1/f_mf_p$	5.0/3.8	0.82	4.7/5.1	1.3
	C-2	$1/f_of_m$	5.0/8.3	0.38	4.7/14.8	0.45
D	C-1	$1/f_m^2$	4.5/1.9	1.47	3.5/3.5	1.40
	C-2	$1/f_of_p$	4.5/3.9	0.36	3.5/6.7	0.37
	C-5	$f_o/f_m^2f_p$	4.5/0.7	2.0	3.5/1.4	1.75
E	C-1	$1/f_mf_p$	5.7/7.2	0.99	3.4/10.0	0.96
F		f_o/f_m^2	5.1/0.9	5.44	4.0/1.3	5.2

(a), (b), (*), (**) See page 117. for details.

Table (25)

See key penultimate page.

Partial Rate Factors for Competitive Defluorination Reactions in Mixtures of Polyfluorobenzenes (1) and (2)

Polyfluorobenzenes (1)/(2)	Site of Attack (1)/(2)	f_i ratio*	$M_{A'}/M_{B'}$**	f_i	$M_{A'}/M_{B'}$**	f_i
			(a)		(b)	
C/F	C-1/C-2	$f_o f_p/f_m$	6.5/1.4	4.75	2.9/1.6	5.05
	C-2/C-1	f_o^2/f_m	15.8/1.4	11.59	9.7/1.6	13.92
E/F	C-1/C-1	$f_o f_p/f_m$	8.9/0.9	5.03	5.7/1.4	4.67
E/D	C-1/C-1	f_p/f_m	10.3/1.3	1.31	6.9/1.7	1.51
	C-1/C-2	f_m/f_o	10.3/3.2	1.06	6.9/5.4	0.95

(a), (b), (*), (**) See page 117. for details.

Table (26)

See key penultimate page.

Partial Rate Factors from Competitive Phenyl Dehydrogenation of 1,2-Difluorobenzene (H) and Polyfluorobenzene ($C_6F_XH_{6-X}$)

			(a)		(b)	
$C_6F_XH_{6-X}$	Site of Attack on $H/C_6F_XH_{6-X}$	f_i ratio*	$M_{A'}/M_{B'}$**	f_i	$M_{A'}/M_{B'}$**	f_i
C	C-3/C-5	$1/f_mf_p$	22.4/8.9	1.58	15.3/15.3	1.41
	C-4/C-5	$1/f_of_m$	15.7/8.9	1.11	13.6/15.3	1.25
D	C-3/C-4	$1/f_of_p$	22.8/9.0	1.57	19.2/13.4	2.0
	C-4/C-4	$1/f_o^2$	16.1/9.0	1.11	13.4/13.4	1.4
E	C-3/C-3	$1/f_of_m$	22.2/19.4	0.72	15.7/27.2	0.82
	C-4/C-3	$f_p/f_o^2f_m$	16.9/19.4	0.55	13.4/27.2	0.7
F	C-3/C-2	f_m/f_of_p	25.6/9.8	2.51	18.8/16.1	2.51
	C-4/C-2	f_m/f_o^2	15.8/9.8	1.55	11.9/16.1	1.6

(continued)

Table (26) (cont.)

$C_6F_XH_{6-X}$	Site of Attack on $H/C_6F_XH_{6-X}$	f_i ratio*	(a)		(b)	
			$M_{A'}/M_{B'}$**	f_i	$M_{A'}/M_{B'}$**	f_i
I	C-3/C-2	f_m/f_o	23.4/8.4	0.94	14.9/11.6	0.97
	C-3/C-4	f_m/f_p	23.4/7.4	2.12	14.9/10.3	2.18
	C-3/C-5	f_o/f_m	23.4/2.7	2.91	14.9/4.2	2.68
	C-4/C-2	$f_m f_p/f_o^2$	13.9/8.4	0.56	7.9/11.6	0.52
	C-4/C-4	f_m/f_o	13.9/7.4	1.26	7.9/10.3	1.16
	C-4/C-5	f_p/f_m	13.9/2.7	1.73	7.9/4.2	1.42
J	C-3/C-2	1	20.3/35.0	0.79	15.4/49.8	0.94
	C-4/C-2	f_m/f_o	12.1/35.0	0.47	9.9/49.8	0.6

(a), (b), (*), (**) See page 117. for details.

Table (27)

See key penultimate page.

Partial Rate Factors for Competitive Phenyldehydrogenation of 1,4-Difluorobenzene [(J); C-2] and Polyfluorobenzene ($C_6F_XH_{6-X}$)

Polyfluorobenzene	Site of Attack on $C_6F_XH_{6-X}$	f_i ratio*	(a)		(b)	
			$M_{A'}/M_{B'}$**	f_i	$M_{A'}/M_{B'}$**	f_i
C	C-5	$1/f_mf_p$	49.1/5.5	2.74	35.9/9.7	2.67
D	C-4	$1/f_of_p$	52.8/8.0	2.01	42.7/12.8	2.29
E	C-3	$1/f_of_m$	59.3/15.6	1.17	32.2/26.8	0.83
F	C-2	f_m/f_of_p	55.3/7.7	3.38	44.5/14.2	3.32
H	C-3	1	49.8/15.4	1.06	35.5/20.3	1.27
	C-4	f_m/f_p	49.8/9.9	1.65	35.0/12.1	2.11
I	C-2	f_m/f_o	47.9/5.9	1.34	36.5/11.5	1.18
	C-4	f_m/f_p	47.9/6.4	2.46	36.5/10.5	2.58
	C-5	f_o/f_m	47.9/3.0	2.63	36.3/4.9	2.76

(a), (b), (*), (**) See page 117 for details.

Table (28)

See key penultimate page.

Partial Rate Factors from Competitive Phenyl Dehydrogenation Reactions of Mixtures of Polyfluorobenzene (1) and (2)

Polyfluorobenzenes (1)/(2)	Site of Attack (1)/(2)	f_i ratio*	(a)		(b)	
			$M_{A'}/M_{B'}$**	f_i	$M_{A'}/M_{B'}$**	f_i
C/F	C-5/C-2	f_m^2/f_o	16.3/13.0	1.28	9.8/20.8	1.08
C/I	C-5/C-2	$f_m^2 f_p/f_o$	8.2/8.4	0.35	4.9/13.6	0.29
	C-5/C-4	f_m^2	8.2/7.0	0.84	4.9/12.4	0.64
	C-5/C-5	$f_o f_p$	8.2/3.3	0.89	4.9/5.6	0.7
E/F	C-3/C-2	f_m^2/f_p	30.7/8.9	3.52	20.8/15.9	3.0
E/D	C-3/C-4	f_m/f_p	34.1/9.0	2.5	22.2/14.1	2.36
E/I	C-3/C-2	f_m^2	28.7/10.2	1.0	17.8/13.7	1.04
	C-3/C-4	$f_o f_m^2/f_p$	28.7/10.9	1.88	17.8/13.0	2.2
	C-3/C-5	f_o^2	28.7/5.6	2.74	17.8/5.5	2.6

(a), (b), (*), (**) See page 117. for details.

Details of Tables (23)-(28)

(a) 3 ml principal polyfluorobenzene : 2 ml competing polyfluorobenzene ($C_6F_XH_{6-X}$)

(b) 2 ml principal polyfluorobenzene : 3 ml competing polyfluorobenzene ($C_6F_XH_{6-X}$)

(*) Subscripts refer to fluorine substituents

(**) $$\frac{M_{A'}}{M_{B'}} = \frac{\text{Yield of Polyfluorobiphenyl from attack at specified site of principal polyfluorobenzene}}{\text{Yield of Polyfluorobiphenyl from attack at specified site of } C_6F_XH_{6-X}}$$

Yield - (Moles of biaryl per mole of peroxide decomposed) x 100

II. 5 The Decomposition of Phenylazotriphenylmethane (PAT) in Hexafluorobenzene

Phenylazotriphenylmethane (prepared as described in Section II. 1.6) was decomposed in hexafluorobenzene using the following experimental method. A weighed amount of PAT (1.0 g) was dissolved in hexafluorobenzene (10 ml), one or two small lumps of carbon dioxide were added to the solution which was then warmed to 80 ± 1°c. The reaction was allowed to proceed at this temperature for 24 hrs. At the end of this period the excess hexafluorobenzene was distilled off (water bath) and the resulting residue was exhaustively steam distilled. The steam volatile products, thus obtained were analysed by ^{19}F n.m.r. spectroscopy [Table (29)] and by gas chromatography-mass spectroscopy [Table (30)].

Table (29)

^{19}F N.M.R. Chemical Shifts of some Steam-Volatile Products from the Decomposition of PAT in Hexafluorobenzene (80 ± 1°c; 24 hrs)

Proposed Assignment	Chemical Shift (ppm)
$C_6F_5.C_6H_5$	F_2, 143.7(143.8); F_3, 162.9(162.8); F_4, 156.2(156.2)
$C_6F_5.C_6H_4.C_6H_5$	F_2, 146.2; F_3, 163.8; F_4, 158.4
$C_6F_5.O.C_6H_5$	F_2, 133.1; F_3, 155.3; F_4, 169.3

Table (30)

Mass Spectroscopic Analysis of the Steam-Volatile Products from the Decomposition of Phenylazotriphenylmethane in Hexafluorobenzene

(80 ± 1°c; 24 hrs)

No.[(a)]	Proposed Assignment	Principal Features of Mass Spectrum (M/e)
1	$C_6H_5OH^{(b)}$	95(4); 94(100); 67(20); 66(16).
2	$C_6H_5.C_6F_5$	245(23); 244(100); 225(19); 224(25); 205(13); 192(8); 175(6); 122(17); (Also peaks at M/e: 112,99,87,76,51,39).
3	$C_6H_5.O.C_6F_5$	261(13); 260(100); 242(24); 232(96); 231(89); 213(36); 193(16); 182(65); 91(22); 77(68); 51(61).
4	$C_6H_5.C_6H_5^{(b)}$	155(6); 154(100); 76(12).
5	$C_6H_5.C_6H_4.C_6F_5$	320(3); 242(7); 182(53); 152(6); 105(100); 77(68); 51(35); (Also peaks at M/e: 305, 301,300,280,269,251,213,203,193,175,165, 135,126,115,98,87,63,57,39).
6	$(C_6H_5)_3CH^{(b)}$	243(19); 244(100); 167(95).
7	$(C_6H_5)_4C$	320(2); 288(13); 243(65); 228(3); 211(50); 183(17); 165(29); 105(100); 77(32); 51(5).

(a) The number refers to the elution order on the G.C. - Mass Spectrograph.

(b) These assignments have been confirmed by a mass spectroscopy library search.

II. 6 The Decomposition of Benzoyl Peroxide in Benzene, Pentafluorobenzene, and Hexafluorobenzene in the Presence of Pentafluoronitrosobenzene

Benzoyl peroxide was decomposed in benzene, pentafluorobenzene or hexafluorobenzene in the presence of pentafluoronitrosobenzene using the technique described in Section (II. 3.1). At the end of the reaction period the excess solvent was removed and the residue was steam distilled (see II. 3.2). The resulting products were analysed by ^{19}F n.m.r., gas chromatographic and g.c.- mass spectrometry techniques. Table (31) lists the yields and ^{19}F n.m.r. analysis, and Table (32) shows the g.c. - mass spectroscopic analysis of some of the steam-volatile products observed in the hexafluorobenzene system.

Table (31)

The Yields and ^{19}F N.M.R. Chemical Shifts of some Steam-Volatile Products from the Decomposition of Benzoyl Peroxide (0.25 g) in Hexafluorobenzene (5 ml) in the Presence of Pentafluoronitrosobenzene (0.2 g)

Proposed Assignment	Yield	δ(ppm, upfield of $CFCl_3$)*
$C_6F_5.C_6H_5$	2.7	F_2, 144.0(143.8); F_3, 162.9 (162.9), F_4, 156.3(156.2)
$C_6F_5.O.C_6H_5$	5.3	F_2, 133.4; F_3, 155.4; F_4, 169.7
$C_6F_5.N(H).C_6H_5$	1.1	F_2, 150.0(149.9); F_3, 163.4(163.3); F_4, 164.1(163.9)
$C_6F_5.N(O).N.C_6F'_5$ (a)	2.3	F_2, 147.0(148.2); F_3, 158.8(160.2); F_4, 148.8(150.3); F'_2, 140.7(141.9); F'_3, 161.9(163.2); F'_4, 153.7(155.2)

(*) Figures in parentheses refer to authentic samples or to literature values.

(a) Ref. 224. The chemical shifts were measured relative to 1,2-dichlorotetrafluorocyclobutene (118.7 ppm upfield of $CFCl_3$).[225]

Table (32)

The G.C.- Mass Spectroscopic Analysis of the Steam-Volatile Products from the Decomposition of Benzoyl Peroxide in Hexafluorobenzene in the Presence of Pentafluoronitrosobenzene

No.*	Proposed Assignment	Principal Features of Mass Spectrum (M/e)
1	Benzoic Acid(a)	122(87); 105(100); 77(64); 51(26).
2	Pentafluorobiphenyl	244(100); (Also peaks at M/e: 224,122 105,77,51).
3	Pentafluorodiphenyl ether	261(5); 260(100); 242(4); 232(70); 231(68).
4	Pentafluoroazoxybenzene(a)	378; (Also peaks at M/e: 359,331,211, 195,190,181,167,131,117).
5	4-Fluorobiphenyl	172(100); standard.
6	Pentafluorodiphenylamine(a)	259(100); 240(12); 122(31); 105(42); 77(37); 51(21).
7	Phenyl Benzoate(a)	198(2); 105(100); 77(32); 51(5).

(*) The number refers to the elution order on the G.C.- Mass Spectrograph.

(a) Compounds also identified as products with benzene and with pentafluorobenzene as solvent.

III. DISCUSSION

III. 1. A Review of The Mechanism of Aryldehydrogenation and Aryldefluorination

It is relevant to review the proposed reaction mechanisms of benzoyl peroxide in (a) benzene, and (b) hexafluorobenzene since these reactions have been most comprehensively studied as examples of aryldehydrogenation and aryldefluorination reactions respectively. These processes are known to occur concurrently during the decomposition of benzoyl peroxide in polyfluorobenzenes and are important in the present work.

1.1 The Decomposition of Benzoyl Peroxide in Benzene

From the kinetics of the reaction (Section I. 2.2)[37-42] and the nature of the products (Section I. 2.1),[9-20,32-35] a reaction scheme has been proposed for the decomposition of benzoyl peroxide in benzenes (Section I. 2.4).[39]

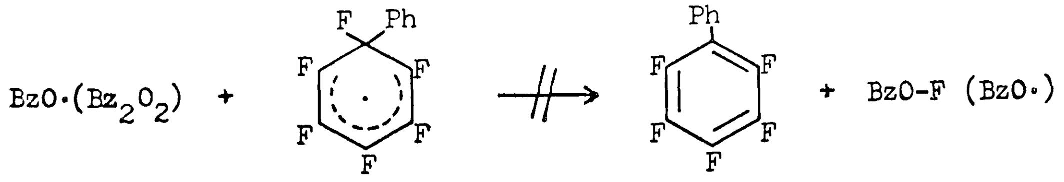
The most important factor in the mechanism is the formation of an intermediate phenylcyclohexadienyl radical ($\sigma\cdot$) from reaction of phenyl radicals, produced by thermolysis of the peroxide, with the solvent. The observed products reflect the fates of this σ-intermediate. The possible modes of reaction are (i) aryldehydrogenation, an oxidation process which may be brought about by benzoyl peroxide and which produces the biaryl components, and alternatively, (ii) the σ-intermediate can react with itself leading to products of dimerization and disproportionation. The extent to which the radical follows either pathway depends on the reaction conditions. By including an oxidation catalyst e.g. oxygen,[44] transition metal compounds[45,46,58-60] or nitro-compounds,$^{3,54-57}$ it is possible to increase aryldehydrogenation at the expense of the radical-coupling reactions.

1.2 The Decomposition of Benzoyl Peroxide in Hexafluorobenzene

The kinetics^{172,173} of, and the products$^{167-172}$ from the decomposition of benzoyl peroxide in hexafluorobenzene parallel those found in the benzene system (Section I, 6.2). As in the benzene system, the formation of an intermediate σ-radical is the most important mechanistic feature. The possible reaction paths of this intermediate are (i) aryldefluorination to produce the biaryl components or (ii) radical-coupling reactions leading to products of dimerization and disproportionation. The difference between the two systems becomes apparent when aromatisation of the σ-complex is considered.

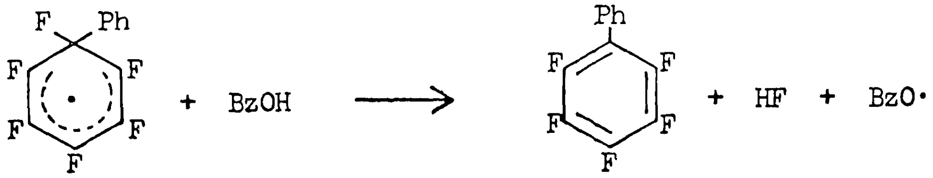
Aromatisation requires the breaking of a C-F bond. This bond is, however, much stronger than the C-H bond and since in the latter case homolysis of the bond to form <u>free</u> hydrogen atoms or molecules is not expected, homolysis of a C-F bond to produce <u>free</u> fluorine atoms or molecules is considered to be even less likely.

The oxidative defluorination of the σ-complex effected by benzoyloxy radicals or benzoyl peroxide (118) was discounted^{175} as an explanation of the formation of high yields of pentafluorobiphenyl in the system since the reaction is endothermic.



(118)

Aryldefluorination of the σ-radical was considered to be possible due to benzoic acid, formed during the reaction, acting as a hydrogen donor to produce hydrogen fluoride as well as the biaryl (119).[178]



(119)

III. 2. The Decomposition of Benzoyl Peroxide in Polyfluorobenzenes

2.1 Polyfluorobiphenyls

2.1.1 In the Absence of Additive

The yields and identities of the steam volatile biaryl products resulting from the the thermal decomposition of benzoyl peroxide in a range of polyfluorobenzenes (80° c, 72-100 hrs) have been reported [Table (3), I. 6.3].[183] These studies have been repeated in the present work [Table (12), II. 3.3]. The two studies compare favourably; there is no greater than a 3% difference in the reported isomer distributions, although larger discrepancies in the total yields of biaryls are sometimes observed.

In the earlier study,[183] the partial rate factors for the phenylation of fluorobenzene (f_{o-F}, 1.62; f_{m-F}, 1.17; f_{p-F}, 0.91) were used to predict the relative rates of attack of polyfluorobenzenes at hydrogen-bearing sites. They were also used to reflect the extent of aryldefluorination when an empirical factor of 0.27 was incorporated. In the di- and tri- fluorobenzenes the agreement between experimental and calculated figures was quite good but greater divergence was found for the more fully fluorinated substrates [Table (3), I. 6.3].

Recently, competitive phenylation reactions between benzene and some mono-substituted aromatic solvents have been carried out with added ferric benzoate.[161] Since there was near-quantitative conversion of the cyclohexadienyl radical to biaryl, it was felt[161] that the partial rate factors determined from these reactions would be more accurate than those from the uncatalysed reactions.

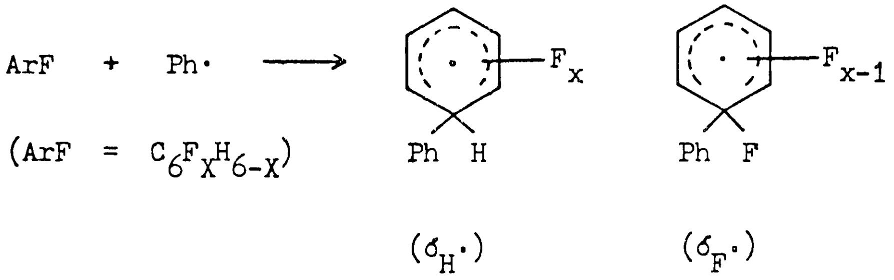
The partial rate factors for the phenylation of fluorobenzene (f_{o-F}, 2.0; f_{m-F}, 1.1; f_{p-F}, 1.1) obtained from these experiments were used to predict the extent of aryldehydrogenation, and also of aryldefluorination with the incorporation of the empirical factor (0.27), in the present study [Table (12) II. 3.3]. Although the values are slightly different from those of the earlier work, the trends are the same.

The partial rate factors for aryldefluorination, deduced by comparing the rates and orientation of attack on hexa- and pentafluorobenzenes (f_{o-F}, 2.47; f_{m-F}, 0.82; f_{p-F}, 1.69),[183] give some indication of the relative rates of aryldefluorination of the tetrafluorobenzenes, but then become rapidly and increasingly less correct in their predictions when applied to less fully fluorinated systems. However, discrepancies have been observed in the partial rate factors calculated for (a) competitive phenylation reactions between pentafluorobenzene derivatives and hexafluorobenzene,[163] and (b) competitive pentafluorophenylation reactions (amyl nitrite with pentafluoroaniline as precursor) of simple aromatic solvents.[162] These were attributed to the formation of complexes between the competing substrates and the radicals or their precursors. This was considered[162,163] to contribute to the selection process causing the additivity principle to fail.

'Complexation' need not be the only explanation for the observed divergences and discrepancies. Any proposal involving differences in relative contributions of the mechanisms for aryldehydrogenation and aryldefluorination will suffice.

The relative rates of aryldefluorination and aryldehydrogenation within the same molecule are conditioned by two terms. One reflects the inherent reactivity of the aromatic site to phenyl radical attack;

the second involves the relative yields of each biaryl from their appropriate radical intermediate. The relative rates of formation of these biaryls may be dependant upon not only the individual rate constants associated with aromatisation ($\underline{k}_H$ and $\underline{k}_F$ below) and the relative concentrations of the two radical intermediates ($\sigma_H\cdot$ and $\sigma_F\cdot$), but also the concentration of the appropriate aromatising reagents.



(120)

(ArF = $C_6F_xH_{6-x}$)

$$\sigma_H\cdot + BzO\cdot\ (Bz_2O_2) \longrightarrow \text{Biaryl (I)} + BzOH\ (+\ BzO\cdot) \qquad (121)$$

$$d[\text{Biaryl (I)}]/dt = \underline{k}_H[\sigma_H\cdot]\,[Bz_2O_2]\ (+\ \underline{k}'_H[\sigma_H\cdot]\,[BzO\cdot]\,) \qquad (122)$$

$$\sigma_F\cdot + BzOH \longrightarrow \text{Biaryl (II)}\ (+\ HF) \qquad (123)$$

$$d[\text{Biaryl (II)}]/dt = \underline{k}_F[\sigma_F\cdot]\,[BzOH] \qquad (124)$$

In the benzoyl peroxide-hexafluorobenzene system, benzoic acid is held to be the essential reagent in the defluorination of the $\sigma_F\cdot$ intermediate.[177] It is thought to be generated, initially, either through phenylation of benzoyl peroxide or from the rearrangement of the $\sigma_F\cdot$ complex leading to the formation of 2,2',3,4,5,6-hexafluorobiphenyl; the bulk, however, is considered to arise from transesterification of tertiary esters (Section I. 6.2).[178]

In the attack of polyfluorobenzenes, in which aryldefluorination and aryldehydrogenation are both modes of reaction, it is suggested that the bulk of the benzoic acid arises from hydrogen displacement [eqn. (121)]. If this is the case, the amount of hydrogen displacement must necessarily be influenced by the relative paucity of available sites. Thus, the yield of benzoic acid formed in this way is considerably less in the phenylation of tetrafluorobenzenes than in that of fluorobenzene. The discrepancies observed through the series may arise from the fall in the concentration of benzoic acid causing a corresponding decrease in the extent to which defluorination can compete with dimerisation as a fate of the intermediate $\sigma_F\cdot$ radical. The failure of the additivity principle in these systems cannot, however, arise from this source. This conclusion is further substantiated by the constancy of the isomer distributions of the biaryls from the decomposition of benzoyl peroxide in pentafluorobenzene at varying reaction times [Table (33)]. Complexation and other factors affecting selectivity in the polyfluorobenzene systems are discussed further in Section (III. 4).

2.1.2 In the Presence of Ferric Benzoate

The addition of ferric benzoate to the reaction of benzoyl peroxide with simple aromatic solvents was found to increase the yields of biaryls greatly, at the expense of tarry residue (I. 3.3).[60] The ferric benzoate was considered to catalyse the oxidation of the σ-complex, and thus, divert it from dimerisation and disproportionation reactions, the routes to the tarry residue. The proposed scheme is set out below:

$$[\mathrm{PhArH}]\cdot + \mathrm{Fe(III)} \longrightarrow \mathrm{PhAr} + \mathrm{H(I)} + \mathrm{Fe(II)} \qquad (125)$$

$$\mathrm{PhCO.O}\cdot + \mathrm{Fe(II)} + \mathrm{H(I)} \longrightarrow \mathrm{PhCO_2H} + \mathrm{Fe(III)} \qquad (126)$$

Table (33)

Biaryl Yields from the Decomposition of Benzoyl Peroxide (0.025 g) in Pentafluorobenzene (5.0 ml) at varying times (80° ± 1 c)

Biaryl	18 hrs		24 hrs		48 hrs		90 hrs	
	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
2,3,4,5-Tetrafluoro-	3.5	9	5.2	9	5.3	10	5.8	9
2,3,4,6-Tetrafluoro-	18.5	48	24.3	49	25.5	48	30.1	48
2,3,5,6-Tetrafluoro-	8.1	21	10.4	21	11.3	21	13.3	22
2,3,4,5,6-Pentafluoro-	8.7	22	10.5	21	11.6	21	12.8	21

(a) (Moles of biaryl per mole peroxide decomposed) x 100.

(b) Isomer distribution %.

Ferric benzoate has also been used in competitive reactions involving benzene and a number of aromatic substrates (I. 5).[159-161] The partial rate factors thus obtained were slightly different from, but in the same relative order as, those for uncatalysed reactions.[143-149]

The addition of ferric benzoate to the reaction of benzoyl peroxide with hexafluorobenzene has no effect on the biaryl yield.[169] This finding is consistent with the proposed mechanism of aryldefluorination[178,180] which does not involve oxidation.

In the present work, the biaryl yields were determined for the reaction of benzoyl peroxide with a number of polyfluorobenzenes in the presence of ferric benzoate. The results are shown in Table (13), Section(II. 3.3).

The only sizable increase in the yields of biaryl from hydrogen-displacement relative to those from fluorine-displacement, when ferric benzoate was added, was found for attack of pentafluorobenzene (10%) and of 1,2,3,4-tetrafluorobenzene (16%). In all the other systems studied the increase was 3% or less. Aryldefluorination appears to be unaffected by the additive; there is no change in the yields of the biaryls from this process or in the orientation of attack. This in turn means that changes in the yield of aryldefluorination products relative to that of aryldehydrogenation products occurs either after the formation of the intermediate complexes ($\sigma_H\cdot$ and $\sigma_F\cdot$) and is associated with their subsequent rearomatisation, or before phenyl radicals have selected their site of attack. Diversion of an incipient intermediate radical does not occur.

2.1.3 In the Presence of Trichloroacetic Acid

p-Fluorobenzoic acid was the first compound that was shown to catalyse the aryldefluorination reaction.[177] When added to the benzoyl peroxide-hexafluorobenzene system, it caused an increase in the yield of 2,3,4,5,6-pentafluorobiphenyl at the expense of 2,2',3,4,5,6-hexafluorobiphenyl and the radical combination products.

The effect of a number of hydrogen donors upon the yield of pentafluorobiphenyl formed by the thermal decomposition of phenylazotriphenylmethane (PAT) in hexafluorobenzene (80°) was later studied.[178] In the absence of hydrogen donors, no pentafluorobiphenyl was observed. However, the hydroxyl groups in phenols and in carboxylic acids were found to provide hydrogen for the aromatisation of the intermediate. No simple relationship was found between the acidity of the additive and the effect upon the yield of biaryl. The influence of the hydrogen donor was thought to involve three factors: (a) the strength of the X-H bond which is broken, (b) the stability of the radical resulting from hydrogen abstraction from the donor and (c) the extent to which the additive diverts phenyl radicals from reaction with hexafluorobenzene. Trichloroacetic acid was the most effective hydrogen donor for the PAT-hexafluorobenzene system.

The yields of biaryls from the decomposition of benzoyl peroxide in polyfluorobenzenes in the presence of trichloroacetic acid are listed in Table (14), Section (II. 3.3). The results show that there is no selective increase in the yields of biaryls resulting from fluorine displacement from the σ-intermediate on addition of the additive. This suggests that the amount of benzoic acid produced in these reactions is sufficient (a) to allow maximum defluorination of the intermediate and, (b) not to be a contribution to the discrepancies in the partial rate factors (III. 2.1.1). It would appear that trichloroacetic acid, and hence benzoic acid, does not promote aryldefluorination over the radical combination reactions. Thus, added acids do not improve the poor (2%) yield of decafluorobiphenyl formed by the pyrolysis of bis(pentafluorobenzoyl) peroxide in hexafluorobenzene,[197] in which dimerisation apparently supercedes all other fates of the radical intermediate.[201,202]

2.2 Polyfluorophenyl Benzoates

2.2.1 In the Absence of Additive

The steam volatile products from the decomposition of benzoyl peroxide in di-, tri- and tetra- fluorobenzenes comprise (as well as polyfluorobiphenyls) some polyfluorophenyl benzoates. The identification of these benzoates is described in Section (II. 3.5.1).

Pentafluorophenyl benzoate was not detected as a product of the reaction of benzoyl peroxide with hexafluorobenzene[178] and no aryl benzoates[182] were observed in the benzoyl peroxide-pentafluorobenzene system. These findings were confirmed in the present work.

The observed esters are listed in Table (16) (II. 3.5). They are formed from attack at fluorine-bearing sites only. No aroyloxydehydrogenation appears to take place, and attack <u>ortho</u>- to fluorine is the preferred orientation of attack.

Aryl benzoates are well known minor products from the reaction of benzoyl peroxide with mono-substituted benzenes.[10-13] They are thought to be formed by reaction of benzoyloxy radicals with the aromatic substrate to give a σ-intermediate (127) which is subsequently dehydrogenated (128).

$$\mathrm{PhCO.O\cdot} + \mathrm{ArH} \longrightarrow [\mathrm{PhCO.O.ArH}]\cdot = (\sigma'\cdot) \qquad (127)$$

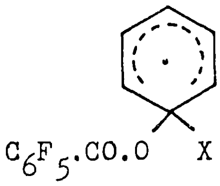
$$(\sigma'\cdot) + (\mathrm{PhCO.O})_2 \longrightarrow \mathrm{PhCO.O.Ar} + \mathrm{PhCO_2H} + \mathrm{PhCO.O} \qquad (128)$$

There is evidence that the formation of this aroyloxycyclohexadienyl radical is reversible,[25,43,48,49] and the ester yield increases on addition of oxidising agents such as oxygen,[24,44] copper salts[45,46] and iodine.[47]

Aryl benzoates are also found as products of the decomposition of bis(pentafluorobenzoyl) peroxide in aromatic solvents (I. 7). In fact, with chlorobenzene and bromobenzene the main product is phenyl pentafluorobenzoate.[195,198] This can only arise by replacement of the chlorine or bromine atom, and it was suggested[180] that, owing to their electrophilicity, pentafluorobenzoyloxy radicals are stabilised by the formation of charge-transfer complexes (129):

$$C_6F_5.CO.O\cdot \quad + \quad :X\text{-}Ph \quad \longrightarrow \quad C_6F_5.CO.O^{-+}X\text{-}Ph \qquad (129)$$

$$C_6F_5.CO.O^{-+}X\text{-}Ph \quad \longrightarrow$$

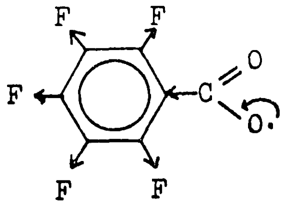


(σ·) (130)

$$\sigma\cdot \quad + \quad \cdot O.CO.C_6F_5 \quad \longrightarrow \quad C_6F_5.CO.OX \quad + \quad C_6H_5.O.CO.C_6F_5 \qquad (131)$$

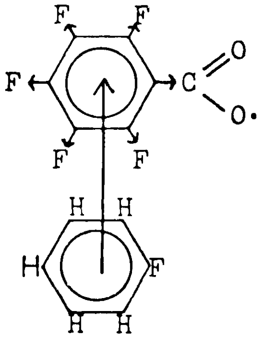
Pentafluorobenzoyloxylation is less, and pentafluorophenylation is greater, in the attack of fluorobenzene than of the other halogenoarenes.[172] This was thought to arise from less charge-transfer stabilisation of the aroyloxy-radical causing more ready decarboxylation, due to the high electronegativity of the fluorine atom. Almost exclusive attack at the fluorine-bearing carbon atom by elecrtophilic pentafluorobenzoyloxy- and pentafluorophenyl-radicals was still found. This was considered to be due to the fluorine inductive effect (-I) withdrawing some of the charge from the aromatic ring and causing the 1-position to be a point of low electron density.

Although stabilisation of the pentafluorobenzoyloxy radical by a charge-transfer complex of the type postulated for chloro- and bromobenzene [eqn. (129)] was considered much less likely in fluorobenzene;[172] some stabilisation must still occur since the powerful inductive effect (-I) of five fluorine atoms in the aryl nucleus would otherwise cause rapid decarboxylation to pentafluorophenyl radicals:



(XXXIV)

This second type of stabilisation was considered to be achieved through the formation of electron-transfer complexes (π-complexes).[172] These have also been postulated [see Section (I. 6.4)] to be formed between 'electron-rich' benzene and 'electron deficient' hexafluorobenzene.

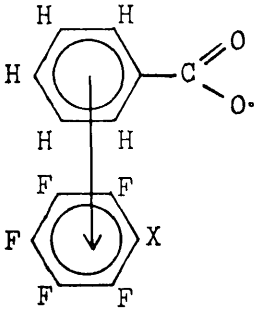


(XXXV)

A study of the decomposition of pentafluorobenzoyl peroxide in a range of polyfluorinated benzenes[199] showed that as the solvent becomes more fully fluorinated less aroyloxylation is observed. This has been attributed[180] to the π-interactions becoming weaker since the difference in polarity of the nuclei of the radicals and of the substrate becomes smaller.

In the reaction of benzoyl peroxide with di-, tri- or tetrafluorobenzenes, the formation of such complexes need not be postulated since there is no discernible trend in the yield of esters through the series that could be attributed to complex formation [Table (16); (II. 3.5)]. The yields appear to reflect the order of activation o-F>p-F>m-F.

In the reactions between benzoyl peroxide and hexafluorobenzene or pentafluorobenzene, where esters are not observed, an electron-transfer complex (XXXVI) may be formed between the benzoyloxy radical and the highly fluorinated benzene. In this case the formation of such a complex would destabilise the benzoyloxy radical, allowing more ready decarboxylation,



(XXXVI) (X = F or H)

partly because of electron withdrawal from the carboxyl fragment and partly because of stabilisation of the phenyl radical.

2.2.2 In the Presence of Ferric Benzoate

Ferric benzoate catalyses the aromatisation of the aroyloxycyclohexadienyl radicals formed in the decomposition of benzoyl peroxide in simple aromatic solvents.[7] The mechanism of catalysis of this ester formation [(132)-(135)] is considered to be the same as that for biaryl formation (I. 3.3).

$$PhCO.O\cdot + ArH \longrightarrow [PhCO.O.ArH]\cdot \qquad (132)$$

$$[PhCO.O.ArH]\cdot + Fe^{3+} \longrightarrow PhCO.O.Ar + H^{+} + Fe^{2+} \qquad (133)$$

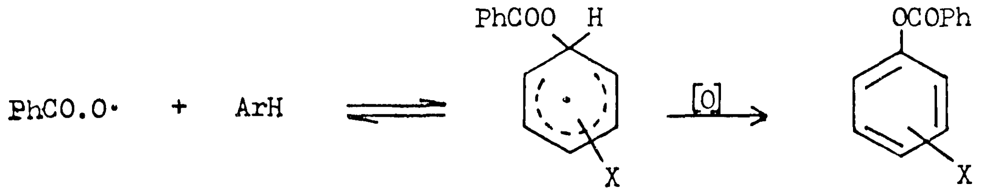
$$PhCO.O\cdot + Fe^{2+} \longrightarrow PhCO.O^{-} + Fe^{3+} \qquad (134)$$

$$PhCO.O^{-} + H^{+} \longrightarrow PhCO_2H \qquad (135)$$

In the polyfluorobenzene systems, ferric benzoate does not have as great an effect on the yields of biaryls from hydrogen-displacement, as that found in the simple aromatic solvents,[60,161] and it has no effect on the yields of biaryls from fluorine-displacement. Ferric benzoate does, however, cause a reduction in the yield of esters

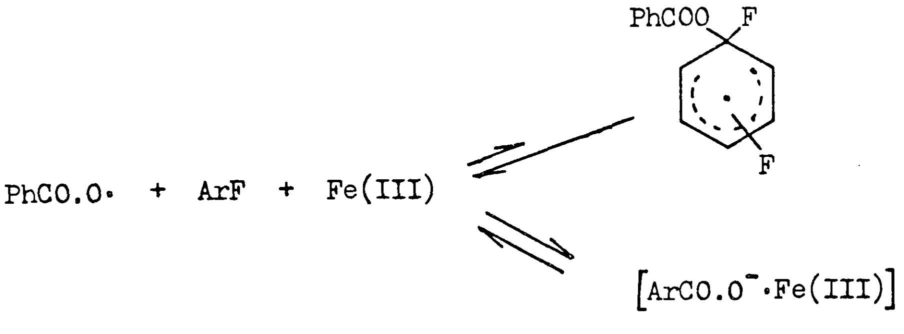
[(II. 3.5.2); Table (16)] formed by fluorine displacement in polyfluorobenzenes.

Reversibly-formed complexes between aroyloxy radicals and arenes (136) have been detected [(I. 2,3); CIDNP studies][48,49] in similar systems.



(136)

The iron (III) salt may, by competing with the substrate, remove benzoyloxy radicals [cf. Cu(II) salts][45] and therefore diminish the chance of forming the aroyloxycyclohexadienyl intermediate necessary for ester formation (137).

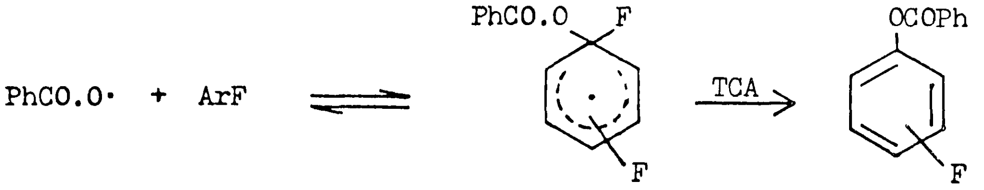


(137)

2.2.3 <u>In the Presence of Trichloroacetic Acid</u>

Trichloroacetic acid has no effect on the yields or relative yields of biaryls formed by phenyldefluorination in the reactions of benzoyl peroxide with any polyfluorobenzenes, other than hexafluorobenzene (III. 2.1,3). However, it promotes ester formation in these substrates quite considerably [Table (16); (II. 3.5.2)].

This finding may be explained by the reversible formation of aroyloxycyclohexadienyl intermediates. Trichloroacetic acid (TCA) is a stronger hydrogen donor than benzoic acid,[179] and may enhance aroyloxydefluorination allowing ester formation to compete more favourably with the breakdown of, or other fates (e.g. radical coupling reactions) of, the radical intermediate.



(138)

III. 3 The Further Decomposition of Residue from the Reaction of Benzoyl Peroxide with 1,3,5-Trifluorobenzene and 1,2,3,4-Tetrafluorobenzene

The non-steam volatile residues obtained from the decomposition of benzoyl peroxide, in either the absence or the presence of additives (ferric benzoate or trichloroacetic acid), were dissolved in benzene and allowed to decompose further at 80°c, the resulting products obtained by steam distillation being then analysed by mass spectroscopy [Tables (17) and (18); (II. 3.6)]. The total yield of these steam-volatile products was found to be no more than 5% (G.L.C.) of that of the original aromatisation products (the biaryls and esters). This, however, does not represent the total decomposition of the residue. Although some differences in the relative yields of products, from one solvent, were found for the three samples [(1) with no additive; (2) with added ferric benzoate; and (3) with added trichloroacetic acid], the main components were the same. No further yields of biaryls were found in any of the reactions. This is contrary to the observation[174,175] of further yields of pentafluorobiphenyl being obtained by further pyrolysis of the residue from the decomposition of benzoyl peroxide in hexafluorobenzene. It does indicate, however, that the observed yields and relative yields of biaryls from the decomposition of benzoyl peroxide in the polyfluorobenzenes studied (II. 2) are correct.

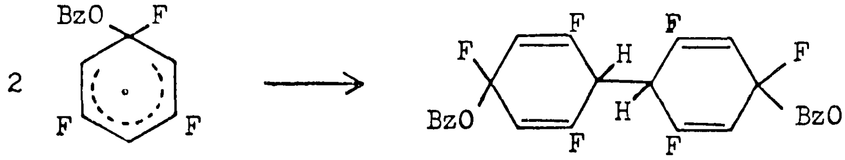
3.1 1,3,5-Trifluorobenzene Phenylation Residue

3.1.1 Benzoic Acid

Benzoic acid was one of the major steam-volatile components of the residue. This is to be expected since a number of esters are likely in the system. They may be formed by the reaction of benzoyloxy radicals or benzoyl peroxide with other reactants [for example, reaction (140)] or by cyclohexadienyl

$$\sigma_F\cdot \ + \ BzO\cdot \ (Bz_2O_2) \longrightarrow \sigma_F\text{-}OBz \ (+BzO\cdot) \qquad (140)$$

radical coupling reactions [e.g. reaction (141)].



(141)

$(\sigma_F\cdot)$

Pyrolysis of these and other similarly formed adducts will yield benzoic acid.

3.1.2 Biphenyl Carboxylic Acid

The molecular weight (198) and the mass spectroscopy fragmentation pattern of the observed product was the same as that found for phenyl benzoate; the gas chromatographic retention time, however, recommends the assignment of biphenyl carboxylic acid. This may be formed by the phenylation of benzoyl peroxide [(142) and (143)].

$$C_6H_5\cdot \ + \ C_6H_5CO.O.O.COC_6H_5 \longrightarrow C_6H_5C_6H_4COO\cdot \ + \ C_6H_5COO\cdot \qquad (142)$$

$$C_6H_5C_6H_4COO\cdot \begin{array}{l} \longrightarrow C_6H_5C_6H_4COOH \\ \longrightarrow C_6H_5C_6H_4\cdot \\ \qquad\ \ \text{(XXXVII)} \end{array} \qquad (143)$$

Arylation of benzoyl peroxide would be expected in concentrated solutions where the ratio of solvent to peroxide is less, or in solutions in which the solvent is unusually inert. p-Phenyl benzoic acid has been isolated during the decomposition of benzoyl peroxide in concentrated solutions.[226] Pentafluoroterphenyl has been observed as a product of the decomposition of benzoyl peroxide in hexafluorobenzene.[181] Evidence points to this being formed by the attack of biphenylyl radicals (XXXVII) on the solvent.

3.1.3 Terphenyls

The steam volatile residue appears to contain several isomeric terphenyls [Table (17); (II. 3.6)]. In the decomposition of benzoyl peroxide in benzene, p-terphenyl was shown to be formed by the further phenylation of the biphenyl product (144).[36]

$$C_6H_5\cdot \quad + \quad C_6H_5.C_6H_5 \quad \xrightarrow{[-H\cdot]} \quad p\text{-}C_6H_5\cdot C_6H_4\cdot C_6H_5 \tag{144}$$

It has been suggested[181] that terphenyls observed in the hexafluorobenzene-benzoyl peroxide system are formed by the reaction of biphenylyl radicals upon the solvent [reactions (145) and (146)],

$$C_6H_5.C_6H_4\cdot \quad + \quad C_6F_6 \quad \longrightarrow \quad [C_6H_5.C_6H_4.C_6F_6]\cdot \tag{145}$$

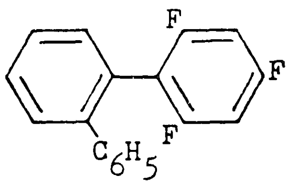
$$[C_6H_5.C_6H_4.C_6F_6]\cdot \quad \xrightarrow{[-F\cdot]} \quad C_6H_5.C_6H_4.C_6F_5 \tag{146}$$

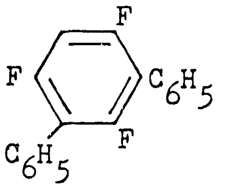
the biphenylyl radicals being formed by prior phenylation of a source of phenyl radicals [e.g. benzoyl peroxide; reactions (142) and (143)]. Terphenyls may also arise from radical-radical combination reactions involving arylcyclohexadienyl and phenyl radicals [reaction (147)].

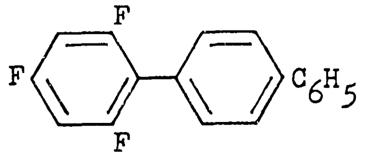
$$[ArPhH]\cdot \quad + \quad Ph\cdot \quad \longrightarrow \quad Ar.C_6H_4.Ph \tag{147}$$

Two isomeric trifluoroterphenyls were observed for the 1,3,5-trifluorobenzene system. These have been designated as

2,4,6-trifluoro-o-terphenyl (XXXVIII) and 2',4',6'-trifluoro-m-terphenyl (XXXIX). 2,4,6-Trifluoro-p-terphenyl (XL) is another possible isomer. Terphenyl (XXXIX) is only likely to be formed by the further phenylation of the biaryl. Terphenyls (XXXVIII) and (XL) may arise from either further phenylation of the biaryl or biphenylyl radical attack on the solvent.

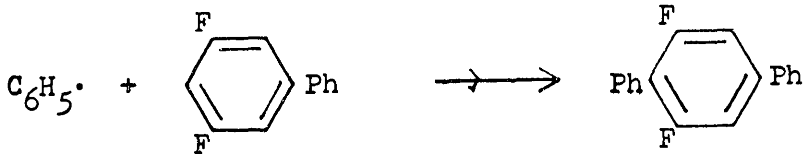

(XXXVIII)


(XXXIX)


(XL)

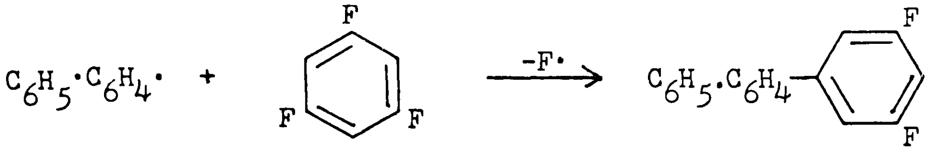
Since hydrogen displacement is much easier than fluorine displacement in 1,3,5-trifluorobenzene [see Table (12) (II. 3.3)] its reactions are likely to parallel those of benzene rather than those of hexafluorobenzene. This points to phenylation of biaryls being the preferred mode of formation of terphenyls, although the observation of biphenyl carboxylic acid suggests that the formation of biphenylyl radicals cannot be ruled out.

Only one difluoroterphenyl isomer is apparently formed; this has been designated as 2',6'-difluoro-p-terphenyl (XLI), a compound considered to be formed by phenyl radical attack of the already formed difluorobiphenyl (148).

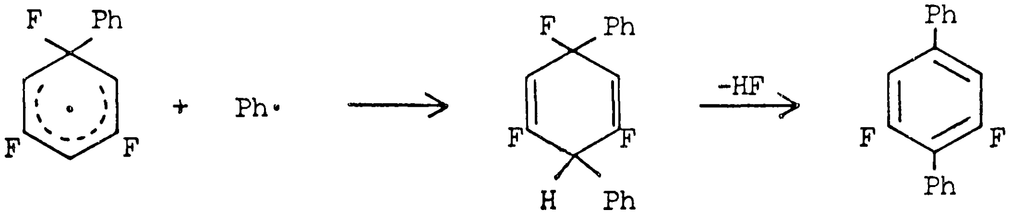

(XLI)

(148)

The attack by biphenylyl radical on the solvent (149), or the radical-radical coupling reaction (150) are considered much less likely since fluorine displacement is much less easy than hydrogen displacement.



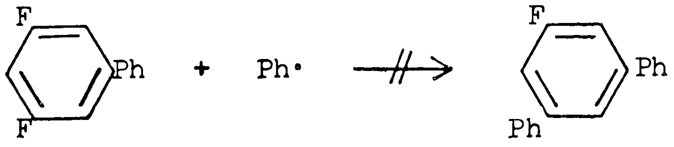
(149)



(150)

(XLI)

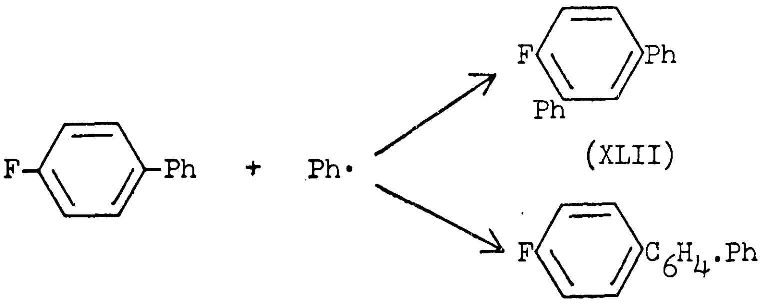
Two fluoroterphenyl isomers are observed as steam volatile products of the residue from the benzoyl peroxide-1,3,5-trifluorobenzene system. Phenyl radical attack at a carbon-bearing fluorine atom on 3,5-difluorobiphenyl (151) is,however, considered unlikely since such an attack would give rise to one isomer only.



(151)

Also, only a relatively small amount of the difluoroterphenyl ester, apparently formed by hydrogen displacement of 2,6-difluorobiphenyl, is observed, whereas the monofluoroterphenyl isomers form a major faction of the steam volatile residue.

4-Fluorobiphenyl was used as a standard for determining the yields of biaryls from the reaction of benzoyl peroxide with 1,3,5-trifluorobenzene. It was placed in the reaction vessel before the decomposition was allowed to proceed. The observed monofluoroterphenyls, assigned to 4'-fluoro-*m*-terphenyl (XLII) and 4-fluoroterphenyl (XLIII), are thus, considered to be produced by phenylation of this added biphenyl (152).



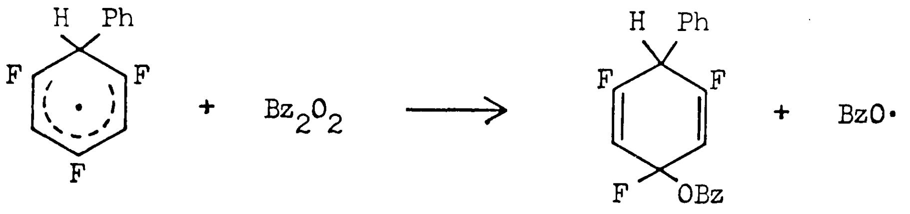
(XLII)

(XLIII)

(152)

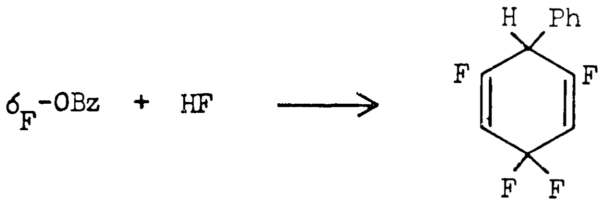
This finding points to errors in the derived yields of biaryls [Tables (12)-(14); (II. 3.3)] formed during the decomposition of benzoyl peroxide in polyfluorobenzenes. The yields of these terphenyls, however, correspond to no more than 3% of the reaction product and will thus impose an error of this magnitude on all the yields of biaryl. It will not affect the biaryl isomer ratios.

A tetrafluoroterphenyl (XLIV) with all four fluorines in one ring [base M/e: 149; Table (17) (II. 3.6)] is also apparently formed. This is not easily explained but may be formed by the attack of a phenyl radical on a fluorinated cyclohexadienyl radical [reaction (155)], this species (σ_FF) being formed originally by a transesterification process [reactions (153) and (154)].



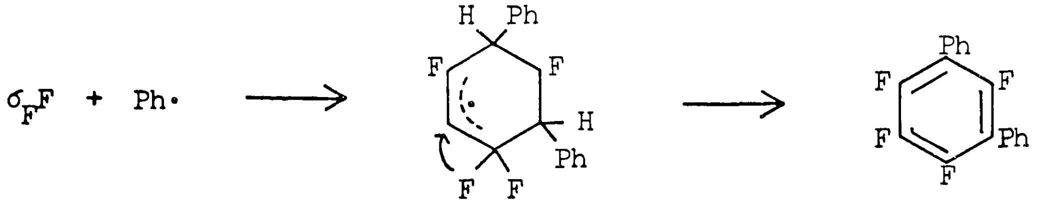
$(\sigma_F\text{-OBz})$

(153)



$(\sigma_F F)$

(154)



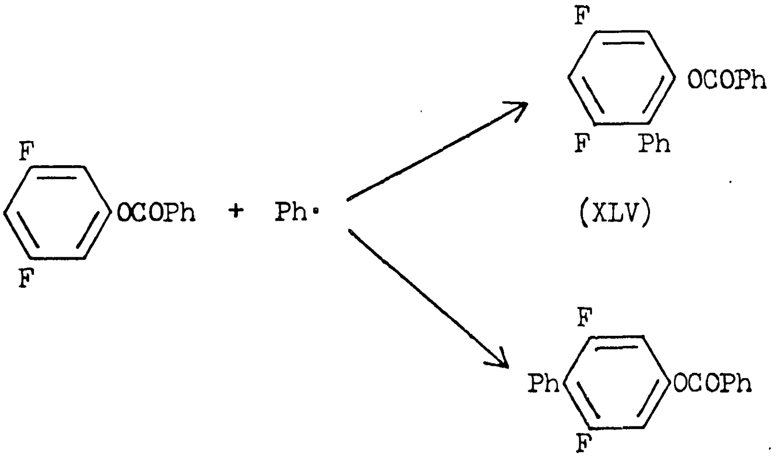
(XLIV)

(155)

A 1,2-fluorine shift necessary to obtain the final product has been postulated in similar systems.[175,201]

3.1.4 Difluorobenzoyloxybiphenyl

3,5-Difluorophenyl benzoate was found to be one of the aromatisation products from the decomposition of benzoyl peroxide in 1,3,5-trifluorobenzene [Table (16), (II. 3.5.2)]. The apparent difluorobenzoyloxybiphenyls (2 isomers) designated as 2,6-difluoro-4-benzoyloxybiphenyl (XLV) and 4,6-difluoro-2-benzoyloxybiphenyl (XLVI) are thought to arise from phenylation of the already formed ester [reaction (156)].

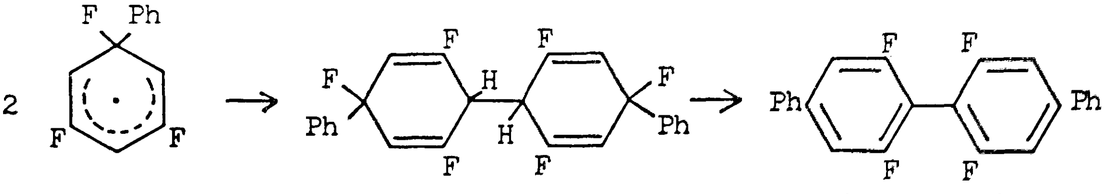

(XLV)

(XLVI)

(156)

3.1.5 Quaterphenyls

Two isomeric compounds (identical top mass) are observed, which have molecular weights corresponding to a tetrafluoroquaterphenyl (M/e: 378). These are considered to be formed by the dimerization of the σ_F-intermediate [reaction (157)].


($\sigma_F\cdot$)

(+ isomers)
(XLVII)

(157)

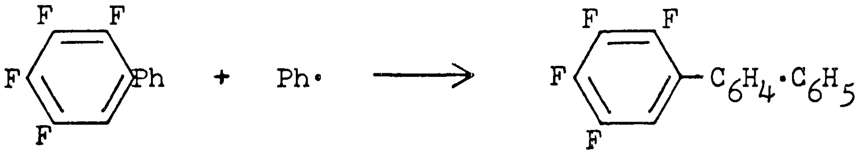
The corresponding hexafluoroquaterphenyls expected from the dimerization of σ_H-radicals are not observed as steam volatile products but this does not exclude them as components of the residue.

3.2 1,2,3,4-Tetrafluorobenzene Phenylation Residues

The steam volatile products of the thermolysis of the residue from the decomposition of benzoyl peroxide in 1,2,3,4-tetrafluorobenzene were analysed by mass spectroscopy [Table (18); (II. 3.6)]. Using this technique it was not possible to distinguish between isomers. Some peaks assigned to compounds may correspond to fragmentations. Some assignments are made because they correspond to those found in 1,3,5-trifluorobenzene [Table (17); (II. 3.6)]. Some compounds, although isomerically different, may be formed in both systems. Others are identified because they correspond to products anticipated in this specific system.

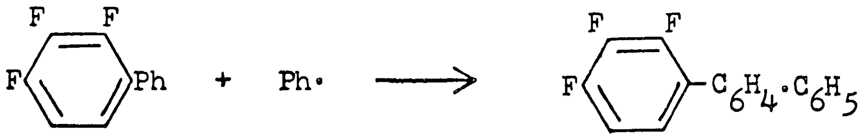
Mass peaks corresponding to benzoic acid, biphenyl carboxylic acid and monofluoroterphenyl are observed. 4-Fluorobiphenyl was used as a standard in the reaction of benzoyl peroxide with 1,2,3,4-tetrafluorobenzene as well as in the 1,3,5-trifluorobenzene system, and so the postulate that monofluoroterphenyl arises from phenylation of this biaryl appears to be confirmed since the successive displacement of three fluorine atoms from the benzene ring is improbable.

Trifluoroterphenyls and tetrafluoroterphenyls are apparently formed in this system. These may arise from the phenylation of the already formed biaryls [reactions (158) and (159)]. Since the reactions



(158)

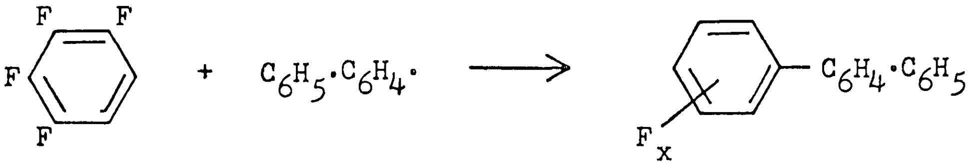
(+ isomers)
(XLVIII)



(159)

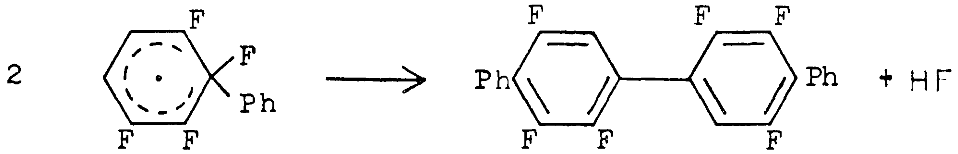
(+ isomers)
(XLIX)

of 1,2,3,4-tetrafluorobenzene are more like those of hexafluorobenzene than are those of 1,3,5-trifluorobenzene [i.e. aryldefluorination occurs more readily; see Table (12), (II. 3.3)] biphenylyl radical attack on the substrate [reaction (160)] may be more important in the more fully fluorinated system.



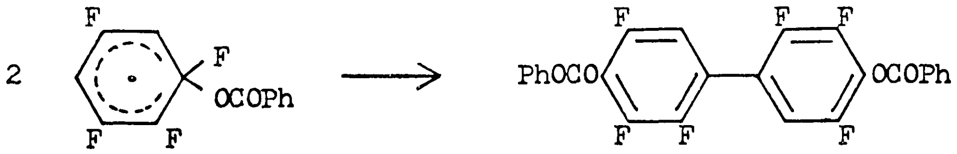
(x = 4 or 3) (L) (160)

Some mass peaks not observed for the attack of 1,3,5-trifluorobenzene have been assigned. Isomeric hexafluoroquaterphenyl is thought to arise from a σ_F-radical dimerisation (161).



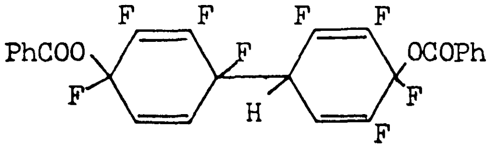
(LI) (161)

There are two possible σ_F-intermediates and so several isomers of (LI) are possible. A radical-radical coupling reaction of the corresponding aroyloxycyclohexadienyl radical (162) is thought to be responsible for the mass peak, M/e; 502.



(+ isomers) (LII) (162)

The top mass (M/e: 522) probably reflects the thermal instability of a dimeric species $[(\sigma'_F)_2]$, such as (LIII), towards dehydrofluorination, since the molecular ion of (LIII), M/e: 542, is not observed.



(LIII)

III. 4 The Competitive Reactions of Benzoyl Peroxide in Mixtures of Polyfluorobenzenes

4.1 Introduction

Partial rate factors have been measured and used successfully to predict the susceptibility of specific nuclear positions, to phenyl radical attack, in many simple aromatic solvents (Section I. 5). They show that in the absence of steric factors, all substituents activate the nucleus towards attack by phenyl radicals, independently of their polar characteristics, in the general order of o-attack > p-attack > m-attack.

The application of measured partial rate factors in polyfluorinated systems has not been so successful.[163,182] This may be attributed to three factors:

(i) Non-ideal behaviour of mixtures of polyfluoroarenes. Hexafluorobenzene forms a 1:1 molecular complex with benzene and its simple derivatives (I. 6.4);[184-192] this species is considered to be a charge-transfer complex in which hexafluorobenzene acts as an electron acceptor. Similar products may arise from the interaction of, for example, o-difluorobenzene and 1,2,3,4-tetrafluorobenzene (a 'lock-and-key' system), as evidenced by measurements of the heats of mixing.[185]

Such interactions may make the mixtures of substrates unhomogenous on the molecular scale, and introduce a third species to the competition in which any reagent has an approximately equal chance of attack upon either component.

(ii) Interaction between fluoroarenes and the radical source.
A similar (charge-transfer) interaction is expected between hexafluorobenzene and the phenyl radical,[163,182,183] and, possibly, with its

precursors such as the benzoyloxy radical or benzoyl peroxide itself. Such a complex would again render the solution unhomogenous, making hexafluorobenzene more susceptible to attack than its stoichiometric concentration would allow; it also affords a second 'stabilised' phenyl radical whose selectivity would by expected to differ from that of the radical formed by decarboxylation of the benzoyloxy radical in the absence of hexafluorobenzene.

(iii) Energetics of displacement of hydrogen and fluorine. Simple competition processes have involved similar kinetic and energetic considerations, i.e. hydrogen displacement allowing the formation of either biaryl. Although the mechanisms of phenylation of benzene and of hexafluorobenzene appear to have common steps, and show similar kinetics so far as the decomposition of benzoyl peroxide in either solvent is concerned, they differ essentially in the processes by which the intermediate complexes regain aromatic stability. Hydrogen is held to be removed by oxidative processes (I. 2.1), whereas fluorine is thought to be removed by sources of 'acidic' hydrogen (I. 6.2); this in addition to the differences of strength of the bonds being broken. As, in each case, biaryl formation is in competition with radical-radical coupling processes, the relative yields of aryldehydrogenation and aryldefluorination products must be conditioned by the rates of a number of disparate processes.

Competitive reactions assume that (i) the mechanism of attack of both substrates is the same, (ii) the mechanism of formation of the analysed products is the same, (iii) the yields and relative yields of products are the same in the presence or absence of the second substrate, (iv) the side products influence neither the course of the selection nor the aromatisation process of each set of intermediates,

(v) the kinetic order of the substitution process is the same for both substrates, and (vi) there are no prior selection processes.

The succesful application of partial rate factors in predicting the reactivities of specific nuclear sites in simple aromatic systems is considered to show that all the above conditions are met adequately.[161]

Competition reactions involving measurement of relative yields of biaryls formed by aryldefluorination and aryldehydrogenation may be considered invalid on the grounds that the mechanisms of these two processes differ. The discrepancies caused by this need not be significant, and some justification for this view comes[182] from the invariance of the isomer distributions of biaryls formed by both hydrogen and fluorine displacement from polyfluorobenzenes whether under competition conditions or not. On the other hand, a factor pointing to the breakdown of the requirements for competition is the need for an empirical term (0.27)[183] to reflect the relative ease of aryldefluorination, and even this term is only successfully applied in the attack of di- and tri-fluorobenzenes. Increasing divergencies occur between calculated and experimental figures in successively more fully fluorinated substrates (III. 2.1.1).

4.2 Conditions of Analysis

In the present work a number of competitive phenylation reactions of polyfluorobenzenes have been carried out (II. 4). The competition between polyfluorobenzenes and benzene was not studied because the most accurate method of measuring the yields of polyfluorobiphenyls was found to be ^{19}F n.m.r. spectroscopy and not g.l.c., necessary to detect biphenyl, the product from benzene. The similarity in retention time of these biaryls, especially of isomers, made gas chromatography an unsatisfactory quantitative analytical tool. However, the signals observed in the ^{19}F n.m.r. spectrum were, generally, well spaced and, even where there was overlap, only one fluorine signal per molecule was involved, and satisfactory quantitative measurements could be made using the other fluorine signals of the biaryl under study. Pentafluorobenzene was not used in any competition reactions because of the number of polyfluorobiaryls formed and the complexity of the spectrum of the mixture, which did not allow the analysis of any further biaryl mixtures formed in competition. For the same reason, only the competition between 1,2,4-trifluorobenzene (six biaryls formed) and hexafluorobenzene could be succesfully studied. The expensive and low yield synthesis of 1,2,3-trifluorobenzene did not allow studies of the phenylation of this solvent. Of the other possible mixtures, some (e.g. 1,2,3,5-tetrafluorobenzene and 1,3,5-trifluorobenzene) were not studied due to coincidence of a biaryl product. With these exceptions, most of the possible combinations of arenes were studied.

4.3 Hexafluorobenzene-Polyfluorobenzene Mixtures

The yields and relative yields of biaryls from the competitive phenylation reactions of hexafluorobenzene with a number of polyfluorobenzenes have been measured [Table (19); (II. 4.2)]. Using the results for aryls produced by fluorine displacement, partial rate factors (f_i) have been determined [Table (23); (II. 4.3)].

The decomposition of benzoyl peroxide in single polyfluorobenzenes [Table (12); (II. 3.3)] provides greater amounts of product than do the competitive reactions where the yields expected can only be $2/5^{ths}$ or $3/5^{ths}$ of that in the absence of a second substrate. Errors may arise in f_i values from these smaller amounts of material, but, when corrected to equimolar proportions, these values should be the same. Reasonable agreement is found [Table (23); (II. 4.3)] for the corrected f_i values. It is not possible, however, to calculate fluorine substituent rate factors (f_o, f_m, f_p), from these values. This failure of the additivity principle shows that the rules for successful competition have not been met.

The amount of biaryls from fluorine-displacement relative to that from hydrogen-displacement decreases in the fluoroarenes in competition with hexafluorobenzene, from that observed in the phenylation of the single solvent [Table (34)]. A change in the biaryl isomer distributions for hydrogen-displacement is also observed (see 1,2- and 1,3-difluorobenzene).

One or more of the three factors mentioned earlier (III. 3.1) may be contributing to these findings.

Charge-transfer complexes of the type found between hexafluorobenzene and benzene,[192] if formed at all in the mixtures under study, would only be expected between hexafluorobenzene and difluorobenzenes. They should, however, be much weaker than those found in the hexafluorobenzene-benzene system, since the donor strength of a difluorobenzene is less.[185] Variations in the heat of mixing of binary combinations of fluorinated benzenes have been interpreted[185] as being caused by contributions from several different kinds of interaction, including charge-transfer. The extent of the contribution of these interactions is different in each fluorocarbon mixture. It is thus felt that the non-ideal behaviour of fluorinated solvent mixtures, although possibly a contributor, can not be the main cause of the divergencies and discrepancies observed in the phenylation of hexafluorobenzene-polyfluorobenzene mixtures.

Table (34)

See key penultimate page.

Isomer Distributions (%) of Biaryls from the Decomposition of Benzoyl Peroxide in Single Polyfluorobenzenes and in Competition with Hexafluorobenzene

Polyfluorobenzene	Biaryl	Isomer Distributions (a)	(b)	(c)
C	5	18	9	9
	6	49	34	39
	2	33	57	52
D	7	9	6	7
	8	29	18	22
	9	3	-	<1
	3	59	76	71
E	10	26	14	13
	4	74	86	87
F	11	8	7	7
	8	92	93	93
G	12	6	<1	6
	13	7	<1	4
	14	<1	<1	3
	7	30	34	29
	6	37	39	39
	10	19	26	19

(continued)

Table (34) (cont.)

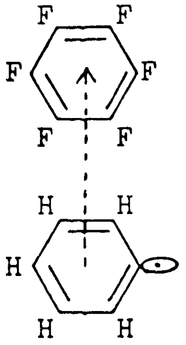
Polyfluorobenzene	Biaryl	Isomer Distributions (a)	 (b)	 (c)
H	15	11	5	8
	16	59	68	65
	14	30	27	27
I	17	-	-	-
	12	39	35	36
	18	39	50	48
	11	22	15	16

(a) Single Solvent

(b) 3 ml C_6F_6 : 2 ml $C_6F_XH_{6-X}$

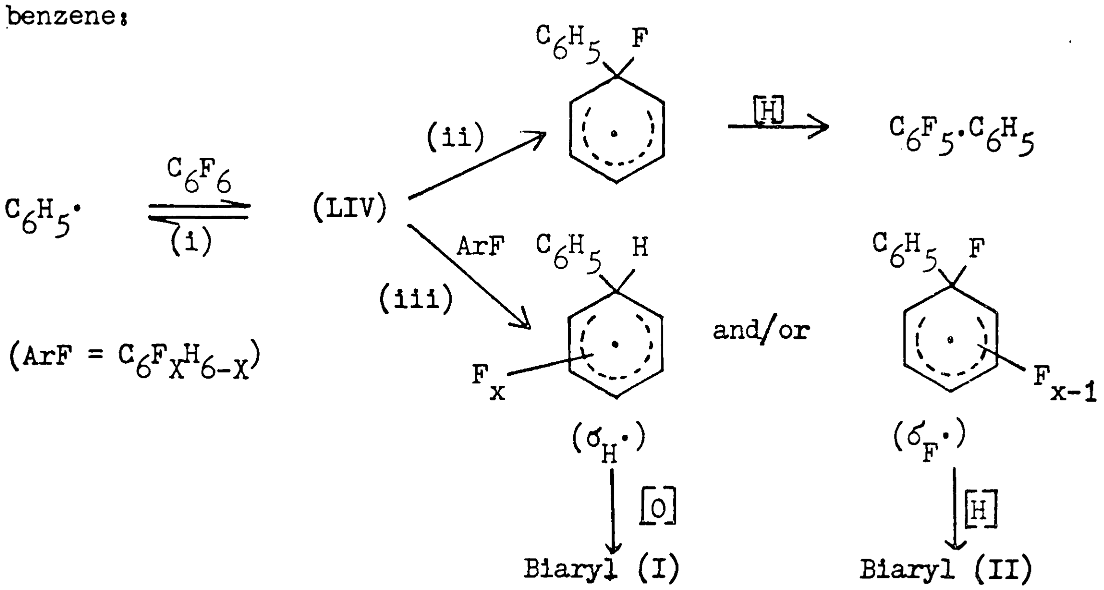
(c) 2 ml C_6F_6 : 3 ml $C_6F_XH_{6-X}$

A charge-transfer complex formed between hexafluorobenzene and phenyl radicals (LIV) has been postulated.[163,182,183]



(LIV)

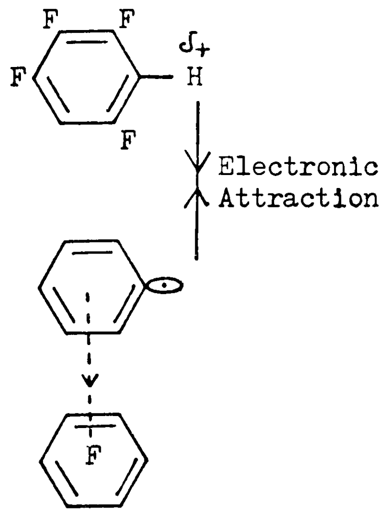
This complex has three plausible modes of reaction (Scheme 6). It may (i) break down into the original components (C_6F_6 and $C_6H_5\cdot$), (ii) collapse to give, eventually, pentafluorobiphenyl, or (iii) react with other species in the system, for example the competing polyfluorobenzene:



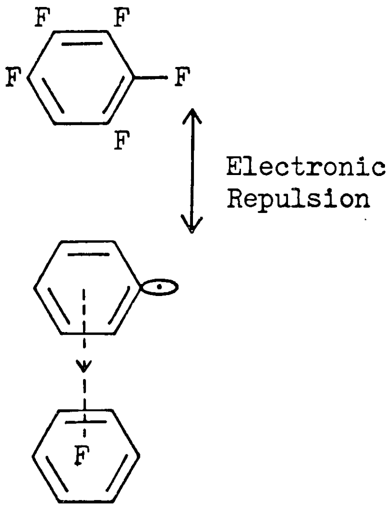
Scheme 6.

The complexed phenyl radical is more stable than the uncomplexed species. By the reactivity-selectivity rule it is expected therefore to be more discriminating between sites on the competing polyfluorobenzene, and, by the Hammond postulate,[227] the transition state associated with the phenylation of arenes would be closer to the structure of the intermediate radical ($\sigma_F\cdot$ or $\sigma_H\cdot$) in the reactions of the complexed phenyl radical. This involves (i) a greater degree of formation of the bond between the radical and the carbon atom under attack, (ii) a consequent shortening of the distance between the two reacting entities, and (iii) a resultant greater contribution by electronic interactions between dipolar substituents in each.

Interactions between the orbital bearing the single electron and the C-F bonds make an orientation such as (LV) preferable, and so encourage aryldehydrogenation. The greater selectivity resulting from complexation correspondingly aids attack at the most activated sites (o- to fluorine) above that already seen in attack by the uncomplexed radical. Both of these factors are shown in the results in Table (34).



(LV)



(LVI)

In the measurement of partial rate factors, the rates and relative rates of formation of biaryl are assumed to reflect the corresponding rates and relative rates of phenyl radical attack on the substrate. The former, however, is governed by the mechanism of aromatisation, whilst the latter is dependent on the relative susceptibility of the specific nuclear positions to attack by phenyl radicals. Since the mechanisms of aryldehydrogenation and aryldefluorination are different, a factor affecting aromatisation may be contributing to the larger disparity in biaryl yields from the two processes in fluoroarenes competing with hexafluorobenzene than that found in the single solvent. In competition reactions, the σ-intermediate from attack of hexafluorobenzene may consume the available benzoic acid to the detriment of aryldefluorination products from the less fully fluorinated arenes. This will also account for the preferential phenylation of hexafluorobenzene.

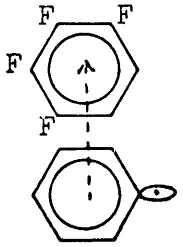
4.4 1,2-Difluorobenzene-Polyfluorobenzene Mixtures

1,2-Difluorobenzene is the simplest polyfluorobenzene in which a measurable amount of phenyldefluorination takes place [Table (12); (II. 3.3)]. Benzoyl peroxide was decomposed in a number of 1,2-difluorobenzene-polyfluorobenzene mixtures. The yields and relative yields of biaryls from these reactions are listed in Table (20) (II. 4.2). Partial rate factors (f_1) were determined (see Section II. 4.3) using the relative yields of biaryls (i) from the competitive aryldefluorination reactions [Table (24); (II. 4.3)] and (ii) from the competitive aryldehydrogenation reactions [Table (26); (II. 4.3)]. In both instances, although reasonable agreement was found between the individual f_1 values of two competing compounds at the two concentration ratios, consistent values of the specific fluorine substituent rate factors (f_o, f_m, f_p) could not be calculated from the set of f_i values found under either arylation condition .

The isomer ratios of biaryls from the phenylation of 1,2-difluorobenzene, alone, and in competition with other polyfluorobenzenes, are listed in Table (35). The amount of aryldefluorination products relative to aryldehydrogenation products is, generally, the same in all systems. The difference in the relative amount of biaryls from hydrogen displacement is, however, smaller in the competitive systems than in the single solvent. This trend is more noticeable in the competitive reactions involving tetrafluorobenzenes than in those involving tri- or di-fluorobenzenes.

Charge-transfer interactions, of the type formed between hexafluorobenzene and benzene,[192] are not expected in those solvent mixtures since the difference in polarity between the components is small. Some kind of solvent-solvent interaction does occur between fluorinated benzenes,[185] most strongly in 'lock-and key' systems (e.g. 1,2-difluorobenzene-1,2,3,4-tetrafluorobenzene). There are differences in the isomer distributions of biaryls from the phenylation of the 1,2-difluorobenzene-1,2,3,4-tetrafluorobenzene system relative to the single systems. These differences, however, are not exclusive to such 'lock-and-key' systems [cf Table (35) and also Table (37) next section].

Charge-transfer complexes between phenyl radicals and the tetrafluorobenzenes (LVII) may be formed. As these are not as strong as the hexafluorobenzene-phenyl radical complexes the effect is less than that observed in hexafluorobenzene-polyfluorobenzene systems (II. 4.3).



(LVII)

Table (35)

See key penultimate page.

Isomer Distributions (%) of Biaryls from the Decomposition of Benzoyl Peroxide in 1,2-Difluorobenzene (H) alone and in competition with other Polyfluorobenzenes

Competing Solvent	Solvent Ratio	Isomer Distribution (%) (15)*	 (16)*	 (14)*
C	(a)	14	46	40
	(b)	12	52	36
D	(a)	10	53	37
	(b)	10	53	37
E	(a)	11	48	41
	(b)	12	50	38
F	(a)	12	54	34
	(b)	11	55	34
I	(a)	7	61	32
	(b)	7	58	34
J	(a)	13	53	34
	(b)	12	55	32

* — Biaryl number (see key)

(a) 3 ml 1,2-$F_2C_6H_4$: 2 ml $C_6F_XH_{6-X}$

(b) 2 ml 1,2-$F_2C_6H_4$: 3 ml $C_6F_XH_{6-X}$

Tetrafluorobenzene-phenyl radical complexation may be a cause of the divergencies observed between experimental and calculated isomer distributions (III. 2.1.1) of biaryls formed by the phenylation of these solvents. Complexed phenyl radicals are, however, expected to be more selective in their attack, the result of this in 1,2-difluorobenzene being increased attack at the most activated site [_o_- to fluorine; _cf_ Table (34); (III. 4.3)]. This is not observed [Table (35)].

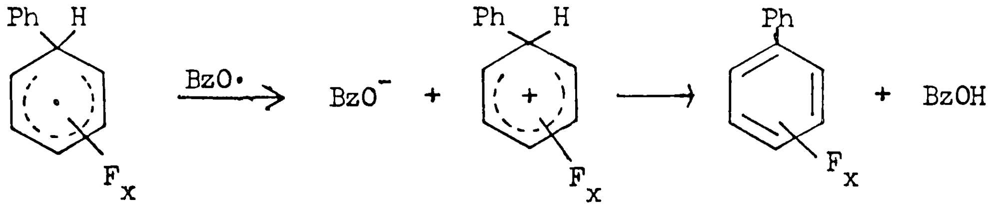
The general spread of the isomer distributions of biaryls from the competitive phenylation of 1,2-difluorobenzene [Table (35)] suggests that complexation, either between competing solvents or between solvent and phenyl radicals or their precursor, is not important in these systems.

The values of f_i shown in Table (24)(II. 4.3) demonstrate that the derived specific rate factors (f_o, f_m, f_p) are not consistent. This inconsistency is more pronounced with increased substitution of the competing fluoroarene. Greater susceptibility to activation or deactivation in more fully fluorinated systems (see also, divergencies in the non-competitive systems III. 2.1.1) suggests a more polar contribution to the total process by which biaryls are formed.

The mechanism of the aromatisation step has been mentioned [III. 3.1 (iii)] as a source of differences between aryldefluorination and aryldehydrogenation processes, and, hence, a contributor to the breakdown of the additivity principle.

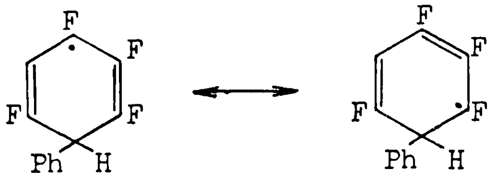
$$\sigma^{\cdot} \longrightarrow \text{Biaryl} \qquad (163)$$

Cadogan _et al_.[102] have suggested that in the reaction of _N_-nitrosoacetanilide (a phenyl radical precursor) with benzene, the chain process involves a redox reaction of the intermediate cyclohexadienyl radical with a diazonium cation (I. 5.3, Scheme 4). The detailed mechanism of the oxidation of the σ_H intermediates in the reaction of benzoyl peroxide with aromatic solvents may also be postulated as involving a one electron oxidation of $\sigma_H\cdot$ to σ_H^+.



(164)

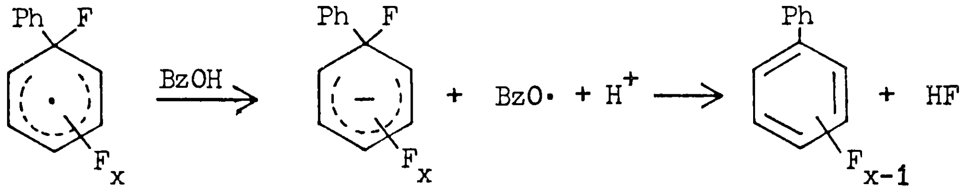
Such an electron loss occurs less readily from carbon atoms which are electron-poor by virtue of their fluorine substituents, and, in some instances, no canonical structure exists in which the unpaired electron can avoid such a carbon atom [e.g. with 1,2,3,5-tetrafluorobenzene as solvent, structures (LVIII) and (LIX)].



(LVIII) (LIX)

A polar contribution therefore becomes added to the individual constraints defining reactivity in those free radical arylations, and is seen in, for example, the considerable diminution of reactivity of tetrafluorobenzenes relative to 1,2-difluorobenzene [Table (26)].

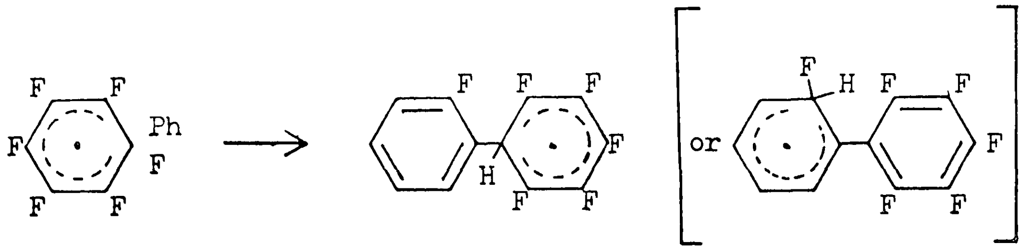
The aryldefluorination reaction may likewise be postulated to involve a redox reaction, but with donation of an electron to the intermediate cyclohexadienyl radical leading to an arylcyclohexadienyl anion ($\sigma_F\cdot$ to σ_F^-):


(165)

An intermediate anion of this type will be more stable with increased fluorine substitution in the aromatic ring. This may allow increased aryldefluorination above that predicted (III. 2.1.1) in more fully fluorinated systems.

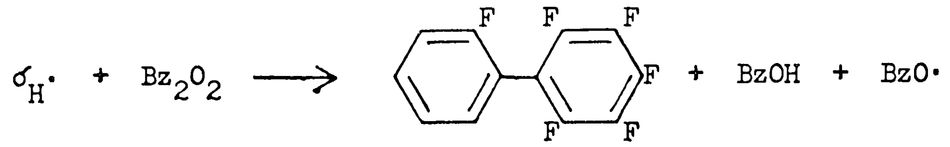
The kinetics of decomposition of aroyl peroxides in simple hydrocarbons associate the formation of biaryls with two oxidative processes involving, respectively, the aroyloxy-radical or the peroxide itself.[38-42] The latter process is more usual, but depends upon an induced decomposition of the peroxide by the radical intermediate.[40] The relative contribution of this process in each system depends upon the concentration of both reactants. The associated rate constants, where they have been measured, vary over a considerable range. For example, the 1.5 order induced decomposition rate constant for benzene is 3.74×10^{-5} mole$^{-0.5}$ l$^{0.5}$ sec^{-1};[40] the figure for benzene-nitrobenzene (100:1 v/v) is 6.5×10^{-5} mole$^{-0.5}$ l$^{0.5}$ sec^{-1}.[41] In some cases, for example chlorobenzene,[39] the order of the rate constant changes from a 1.5 order to a first order process with increasing initial concentration of benzoyl peroxide.

A 1.5 order induced decomposition of benzoyl peroxide ($k_{1.5} = 1.52 \times 10^{-5}$ mole$^{-0.5}$ l$^{0.5}$ sec^{-1})[172] is also observed in hexafluorobenzene. Two processes were thought to contribute to this induced decomposition.[173] One was the rearrangement of $\sigma_F\cdot$ to $\sigma_H\cdot$ [reaction (166)] with subsequent dehydrogenation of the latter, reaction (167).



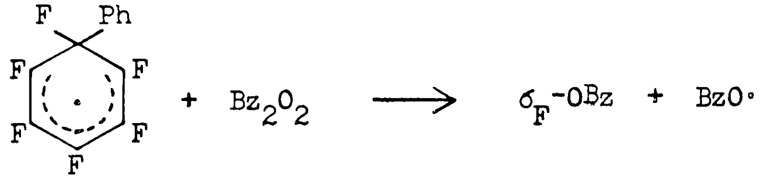
($\sigma_F\cdot$) ($\sigma_H\cdot$)

(166)



(167)

The other was the formation of the ester σ_F-OBz i.e.



($\sigma_F\cdot$)

(168)

The kinetics of the decomposition of benzoyl peroxide in poylfluorobenzenes has not been studied. However, extrapolating from the simple hydrocarbon systems and from hexafluorobenzene as solvent, an induced decomposition of benzoyl peroxide in polyfluorobenzenes is expected, with contributions from processes (168) and (169).

$$\sigma_H\cdot + Bz_2O_2 \longrightarrow PhAr + BzOH + BzO\cdot \qquad (168)$$

$$\sigma_F\cdot + Bz_2O_2 \longrightarrow \sigma_F\text{-OBz} + BzO\cdot \qquad (169)$$

Another smaller contribution to the induced decomposition of benzoyl peroxide may come from its reaction with aroyloxycyclohexadienyl radicals $[\sigma_F\cdot']$

$$\sigma_F\cdot' + Bz_2O_2 \longrightarrow \sigma_F'\text{-OBz} + BzO\cdot \qquad (170)$$

Reaction (171) is not expected however, since the intermediate ($\sigma_H\cdot'$), if it is formed at all, does not react with benzoyl peroxide since no evidence of the corresponding aryl benzoate is observed in the polyfluorobenzene systems studied (III. 2.2).

$$\sigma_H\cdot' \ + \ Bz_2O_2 \ \longrightarrow \ PhCOOAr \ + \ BzOH \ + \ BzO\cdot \qquad (171)$$

The relative contributions of processes (168), (169) and (170) to the induced decomposition of benzoyl peroxide will vary in differing polyfluorobenzene solvents. The amount of aryldehydrogenation, which depends on this induced decomposition, will be affected by contributions from reactions (169) and (170). These are likely to be greater in more fully fluorinated systems and this may be a factor in decreased aryldehydrogenation, from that predicted by partial rate factors (III. 2.1.1), in these systems.

4.5 Other Polyfluorobenzene Mixtures

Benzoyl peroxide was decomposed in a number of binary mixtures of polyfluorobenzenes other than those considered in the preceding two sections. The yields and relative yields of biaryls obtained from these competitive phenylation reactions are listed in Tables (21) and (22) (II. 4.2.) As with the previously discussed systems (III. 4.3 and 4.4), the individual f_i values from the two solvent ratios, determined for aryldehydrogenation [Tables (27) and (28) (II. 4.3)] and for aryldefluorination [Table (25) (II. 4.3)], are in reasonable agreement, but consistent specific rate factors cannot be derived from these f_i values.

Generally, the biaryl isomer distributions are the same for the non-competitive and the competitive (except with C_6F_6) phenylation reactions of the di-, tri and tetra-fluorobenzenes under study.

For some polyfluorobenzenes studied there is no greater than a 3% difference in the isomer distributions [Table (36)], which is within experimental error (II. 3.3.2). For others, [Tables (37) and (38)] some discrepancies are observed, but, due to their randomness, these are not easily explained. They may be caused by some non-specific interactions between the particular competing solvents.

The results of these competitive phenylation reactions substantiate the findings for the 1,2-difluorobenzene-polyfluorobenzene systems (previous section). There is no real evidence of complex formation between competing solvents, or between solvents and phenyl radicals or their precursors. However, inconsistent specific rate factors point to complexities in the mechanisms of biaryl formation. Two possible causes have been postulated (III. 4.4). The first involves contributions from redox reactions of the intermediate cyclohexadienyl radicals. This is consistent with a polar contribution being a factor in the total process of biaryl formation. The second involves the possible variance of the rate constant of the induced decomposition of benzoyl peroxide in differing polyfluorobenzene solvents and solvent mixtures, caused by differences in the amount of the contribution of several processes [(168) - (170); (III. 4.4)] to the induced decomposition. The effect of this is to vary the concentration of benzoyl peroxide available for aryldehydrogenation.

Table (36)

See key penultimate page.

Biaryl Isomer Distributions (%) of Some Polyfluorobenzenes

Polyfluorobenzene	Biaryl	Isomer Distribution (%)
E	10	25 ± 2
	4	75 ± 2
F	11	8 ± 2
	8	92 ± 2
I	17	-
	12	39 ± 2
	18	42 ± 3
	11	19 ± 3
J	19	<2
	13	>98

Table (37)

See key penultimate page.

Biaryl Isomer Distributions from Competitive Phenylation Reactions of 1,2,3,4-Tetrafluorobenzene (C)

Competing Solvent	Solvent Ratio	Isomer Distribution (%) (5)	 (6)	 (2)
None	-	18	49	33
F	(a)	13	43	44
	(b)	17	41	42
H	(a)	18	40	42
	(b)	14	42	44
I	(a) and (b)	16	49	35
J	(a) and (b)	17	48	35

(a) 3 ml 1,2,3,4-$F_4C_6H_2$(C) : 2 ml $C_6F_XH_{6-X}$

(b) 2 ml 1,2,3,4-$F_4C_6H_2$(C) : 3 ml $C_6F_XH_{6-X}$

Table (38)

Biaryl Isomer Distributions (%) from Competitive Phenylation Reactions of 1,2,3,5-Tetrafluorobenzene

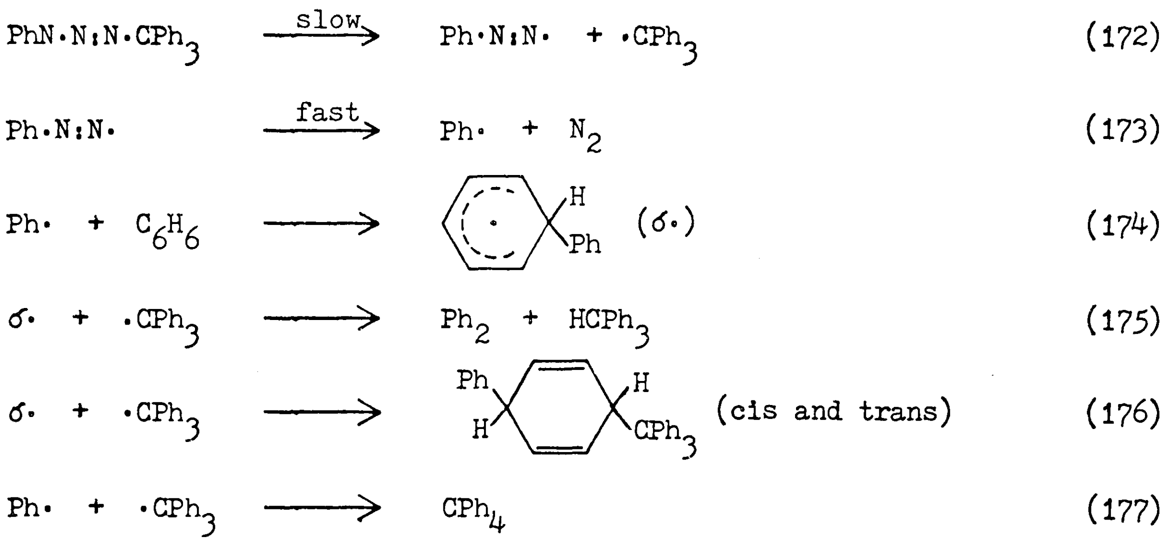
Competing Solvent	Solvent Ratio	Isomer Distribution (%) (7)	(8)	(9)	(3)
None	-	9	29	3	59
E	(a)	10	24	<1	65
	(b)	8	25	<1	66
H	(a)	12	26	<1	61
	(b)	14	27	5	54
J	(a)	15	27	6	52
	(b)	16	27	7	50

(a) 2 ml 1,2,3,5-tetrafluorobenzene : 3 ml competing solvent

(b) 3 ml 1,2,3,5-tetrafluorobenzene : 2 ml competing solvent

III. 5 The Decomposition of Phenylazotriphenylmethane in Hexafluorobenzene

The decomposition of phenylazotriphenylmethane (PAT) in aromatic solvents has been extensively studied (see Section I. 4.4). In benzene PAT decomposes (60-80°) to give mainly triphenylmethane and biphenyl together with some tetraphenylmethane and isomeric 1,4-dihydro-4-triphenylmethylbiphenyls. Kinetic studies established that the decomposition has a first-order rate constant[115] and that there is no chain mechanism.[115-119] No products of dimerisation or disproportionation of the intermediate radical were observed, and the following mechanistic scheme [(172) - (177)] has been proposed.[6]



$$PhN{\cdot}N{:}N{\cdot}CPh_3 \xrightarrow{slow} Ph{\cdot}N{:}N{\cdot} + {\cdot}CPh_3 \qquad (172)$$

$$Ph{\cdot}N{:}N{\cdot} \xrightarrow{fast} Ph{\cdot} + N_2 \qquad (173)$$

$$Ph{\cdot} + C_6H_6 \longrightarrow (\sigma{\cdot}) \qquad (174)$$

$$\sigma{\cdot} + {\cdot}CPh_3 \longrightarrow Ph_2 + HCPh_3 \qquad (175)$$

$$\sigma{\cdot} + {\cdot}CPh_3 \longrightarrow \text{(cis and trans)} \qquad (176)$$

$$Ph{\cdot} + {\cdot}CPh_3 \longrightarrow CPh_4 \qquad (177)$$

The decomposition of PAT in hexafluorobenzene has been studied[179] as a means of determining the effectiveness of hydrogen donors in increasing the yield of pentafluorobiphenyl from the reaction. In the absence of additive no pentafluorobiphenyl was observed as a product. Several hydrogen donors were screened and it was found that the intermediate radical ($\sigma_F\cdot$) did not abstract hydrogen from carbon or from nitrogen even when the resulting radical had considerable resonance stabilisation (e.g. aniline, dibenzyl disulphide, triphenylmethane). However, the hydroxyl groups in phenols and in carboxylic acids provided hydrogen for the aromatisation of the intermediate.

In the present study, the steam-volatile products from the decomposition of PAT in hexafluorobenzene were investigated [see Section II. 5; Tables (29) and (30)].

As with the PAT-benzene system, triphenylmethane was the major product. Other products observed include phenol, biphenyl, pentafluorobiphenyl, pentafluorodiphenyl ether, pentafluoroterphenyl and tetraphenylmethane. No triphenylmethyl fluoride was detected.

5.1 Phenol

The observation of phenol as a product of the decomposition of PAT in hexafluorobenzene is unusual, although its presence can account for other observations in this system that would otherwise be difficult to explain.

No special precautions were taken to exclude oxygen from the reaction vessel since this was found to have no apparent effect on the decomposition of benzoyl peroxide in hexafluorobenzene.[172]

The phenyl radicals generated in the system, reactions (172) and (173), may be trapped by atmospheric oxygen leading to phenol (178).

$$\text{Ph}\cdot + O_2 \longrightarrow \text{Ph-O-O}\cdot \longrightarrow \text{PhOH} \qquad (178)$$

This reaction was proposed to account for the phenol observed as a product of the decomposition of benzoyl peroxide in simple aromatic systems in the presence of added oxygen.[53] Phenyl radicals are not, however, very reactive towards oxygen[52] and a ready source of hydrogen is not obvious in the PAT-hexafluorobenzene system.

Phenol may be produced via the intermediate formation of a peroxide from the reaction of triphenylmethyl radical with oxygen [reactions (179) - (182)].

$$\cdot \mathrm{CPh_3} \xrightarrow{O_2} \mathrm{PhC\text{-}O\text{-}O\cdot} \qquad (179)$$

$$\mathrm{Ph_3C\text{-}O\text{-}O\cdot} + \mathrm{Ph\cdot} \longrightarrow \mathrm{Ph_3C\text{-}O\text{-}O\text{-}Ph} \qquad (180)$$

$$\mathrm{Ph_3C\text{-}O\text{-}O\text{-}Ph} \longrightarrow \mathrm{Ph_3C\text{-}O\cdot} + \mathrm{Ph\text{-}O\cdot} \qquad (181)$$

$$\mathrm{Ph\text{-}O\cdot} + \mathrm{RH} \longrightarrow \mathrm{PhOH} + \mathrm{R\cdot} \qquad (182)$$

(RH = source of hydrogen)

The triphenylmethyloxy radical is more stable, and thus less reactive, than the phenoxy radical but some triphenyl methyl alcohol might still be expected. In the mass spectroscopy analysis a compound with a top mass of M/e: 260 is observed [Table (30); (II. 5)]. The fragmentation pattern, however, is not that which would be expected for triphenyl methyl alcohol. It has been assigned to pentafluorodiphenyl ether. Again, a ready supply of hydrogen, required to make this a feasible reaction path, is not readily available. The presence of some moisture in the system, allowing reactions (183) - (185) to occur, is a possible explanation for the occurrence of products that require hydrogen for their formation.

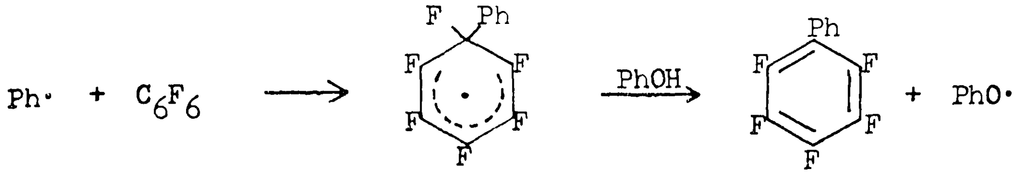
$$\mathrm{Ph\cdot N{:}N\cdot CPh_3} \rightleftharpoons \mathrm{PhN_2^+} + \mathrm{CPh_3^-} \qquad (183)$$

$$\mathrm{PhN_2^+} + \mathrm{H_2O} \longrightarrow \mathrm{PhOH} + \mathrm{H^+} + \mathrm{N_2} \qquad (184)$$

$$\mathrm{CPh_3^-} + \mathrm{H^+} \longrightarrow \mathrm{HCPh_3} \qquad (185)$$

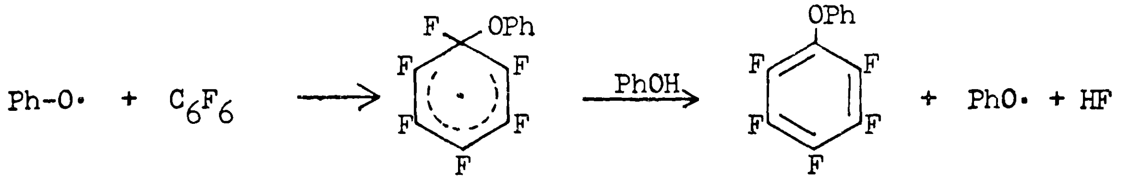
5.2 Polyaryls

The presence of phenol in the system allows the formation of pentafluorobiphenyl, since it acts as a hydrogen donor.[179]



(186)

The phenoxy radical thus formed could attack the hexafluorobenzene leading to pentafluorodiphenyl ether (187).



(187)

A small amount of biphenyl is observed as a product of the decomposition of PAT in hexafluorobenzene. This may arise from a phenyl radical combination reaction (188), or from a biphenylyl radical (190) whose origin (189) is similar to that found in arylation reactions involving benzoyl peroxide.[181]

$$Ph\cdot + Ph\cdot \longrightarrow PhPh \qquad (188)$$

$$Ph^{\circ} + Ph{\cdot}N{:}N{\cdot}CPh_3 \longrightarrow Ph{\cdot}C_6H_4\cdot + N_2 + \cdot CPh_3 \qquad (189)$$

$$Ph{\cdot}C_6H_4\cdot + RH \longrightarrow Ph{\cdot}Ph + R\cdot \qquad (190)$$

(RH = source of hydrogen)

Some pentafluoroterphenyl is also apparently formed in this system. This could arise, possibly, from the further reaction of phenyl radicals with pentafluorobiphenyl (191) or from the attack of biphenylyl radicals on hexafluorobenzene (192).

$$\mathrm{Ph\cdot} \quad + \quad \mathrm{Ph\cdot C_6F_5} \quad \xrightarrow{[-\mathrm{H\cdot}]} \quad \mathrm{C_6H_5\cdot C_6H_4\cdot C_6F_5} \qquad (191)$$

$$\mathrm{Ph\cdot C_6H_4\cdot} \quad + \quad \mathrm{C_6F_6} \quad \xrightarrow{[-\mathrm{F\cdot}]} \quad \mathrm{C_6H_5\cdot C_6H_4\cdot C_6F_5} \qquad (192)$$

Tetraphenylmethane, detected as a minor product may arise from a radical combination reaction involving phenyl and triphenylmethyl radicals . Such a reaction has been postulated in the decomposition of PAT in benzene [reaction (177)].

III. 6 The Decomposition of Benzoyl Peroxide in Benzene, Pentafluorobenzene and Hexafluorobenzene in the Presence of Pentafluoronitrosobenzene

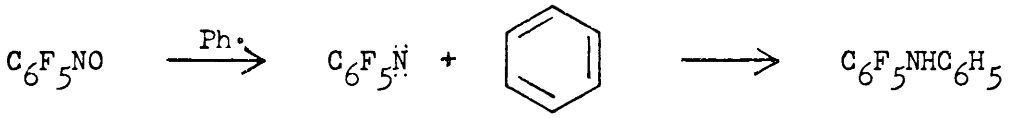
The phenylation, by benzoyl peroxide, of simple aromatic solvents was found to be increased, in the presence of catalytic amounts of nitro-compounds, at the expense of residue.[3,54] The effective catalyst involved in this 'nitro-group' effect is the corresponding nitroso-compound (Section I. 3.2).[57] A number of nitroso-compounds have also been used as trapping reagents for short lived free radicals.[228-230]

In the present study, a catalytic amount of pentafluoronitrosobenzene was found not to have an effect on the yield of pentafluorobiphenyl from the phenyldehydrogenation reaction of pentafluorobenzene. It was considered, however, that the rate of σ-complex formation might be determined if the phenyl radical was trapped by pentafluoronitrosobenzene competing with solvent. Thus, benzoyl peroxide was allowed to decompose (80°) in benzene, pentafluorobenzene or hexafluorobenzene in the presence of pentafluoronitrosobenzene.

The major product from these reactions, was, however, found to be tarry residue. Only small amounts of steam-volatile products (no more than 15% of the amount observed in the uncatalysed reactions) were obtained, and the ^{19}F n.m.r. spectra of these were very complex. Some of the ^{19}F n.m.r. peaks were the same regardless of the solvent used, showing that they arose from reactions of pentafluoronitrosobenzene. The steam-volatile products that have been identified are listed in Tables (31) and (32) (Section II. 6).

The yields of biaryls were drastically reduced (i.e. less than 1% of the yields in the uncatalysed reactions). With pentafluorobenzene as solvent no biaryls were detected at all. Two compounds that have been identified in all three systems, are pentafluorodiphenylamine and decafluoroazoxybenzene. The former is the major component of the steam-volatile faction derived from the benzene system. In the other two solvents it is only a minor product.

Decafluoroazoxybenzene and pentafluorodiphenylamine have been reported[231] as products of the reaction of pentafluoronitrosobenzene with triethyl phosphite $(EtO)_3P$ in benzene at 0°c. In the present study the same reactions may be taking place, phenyl radicals replacing $(EtO)_3P$.



(194)

$$C_6F_5NO + C_6F_5\ddot{N} \longrightarrow C_6F_5(O)N{=}NC_6F_5 \qquad (195)$$

In pentafluorobenzene and hexafluorobenzene the phenyl radical may attack the pentafluoronitrene with donation of a hydrogen from benzoic acid allowing formation of pentafluorodiphenylamine.

With hexafluorobenzene as solvent, pentafluorodiphenyl ether is also apparently formed. When the phenyl radical abstracts oxygen from pentafluoronitrosobenzene, it is possible that the resulting phenoxy radical attacks hexafluorobenzene. This reaction is also postulated to account for the pentafluorodiphenyl ether apparently formed when PAT decomposes in hexafluorobenzene [reaction (186); (III. 5.2)].

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